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JOURNAL AND PROCEEDINGS  
OF THE  
**ROYAL SOCIETY**  
OF NEW SOUTH WALES

FOR

1949

(INCORPORATED 1881)

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VOLUME LXXXIII

Parts I-IV

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EDITED BY

W. B. SMITH-WHITE, M.A., B.Sc.

*Honorary Editorial Secretary*

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THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE  
STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN



SYDNEY

PUBLISHED BY THE SOCIETY, SCIENCE HOUSE  
GLOUCESTER AND ESSEX STREETS

---

Issued as a complete volume, December 6, 1950





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FOR

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OF

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Containing List of Members, Report of Council,  
Balance Sheet, Obituary Notices and Papers read  
in April and May, 1949.

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W. B. SMITH-WHITE, M.A., B.Sc.

*Honorary Editorial Secretary.*

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# Royal Society of New South Wales

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MAR 16 1951



LIST OF THE MEMBERS  
OF THE  
**Royal Society of New South Wales**  
as at April 1, 1949

P Members who have contributed papers which have been published in the Society's Journal. The numerals indicate the number of such contributions.

† Life Members.

**Elected.**

1944		Adamson, Colin Lachlan, Chemist, 36 McLaren-street, North Sydney.
1938	P 2	† Albert, Adrien, D.Sc., Ph.D. <i>Lond.</i> , B.Sc. <i>Syd.</i> , A.R.I.C. <i>Gt. B.</i> , Professor of Medical Chemistry, The Australian National University, 183 Euston-road, London N.W.1.
1935		† Albert, Michael Francois, "Boomerang," Billyard-avenue, Elizabeth Bay.
1898		† Alexander, Frank Lee, Surveyor, 5 Bennett-street, Neutral Bay.
1941		† Alldis, Victor le Roy, I.S., Registered Surveyor, Box 57, Orange, N.S.W.
1948		Anderson, Geoffrey William, B.Sc., 37 Elizabeth-street, Allawah.
1948	P 1	Andrews, Paul Burke, Department of Geology, University of Sydney; p.r. 5 Conway-avenue, Rose Bay.
1930		Aston, Ronald Leslie, B.Sc., B.E. <i>Syd.</i> , M.Sc., Ph.D. <i>Camb.</i> , A.M.I.E. <i>Aust.</i> , Lecturer in Civil Engineering and Surveying in the University of Sydney; p.r. 24 Redmyre-road, Strathfield. (President, 1948.)
1919	P 1	Aurousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah.
1945		Ayscough, Frederick William, B.Sc., 118 Oxford-street, Woollahra.
1935		Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown.
1924	P 2	Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Professor of Experimental Physics in the University of Sydney.
1934	P 2	Baker, Stanley Charles, M.Sc., A.Inst.P., Head Teacher of Physics, Newcastle Technical College, Tighe's Hill; p.r. 8 Hewison-street, Tighe's Hill, N.S.W.
1937		Baldick, Kenric James, B.Sc., 19 Beaconsfield-parade, Lindfield.
1946	P 1	Barclay, Gordon Alfred, Chemistry Department, Sydney Technical College, Harris Street, Ultimo, N.S.W.; p.r. 78 Alt Street, Ashfield.
1919		Bardsley, John Ralph, 76 Wright's-road, Drummoyne.
1947		Beckmann, Peter, A.S.T.C., Lecturer in Chemistry, Technical College, Wollongong.
1933		Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, "Kama," 10 Darling Point-road, Edgecliff.
1926		Bentivoglio, Sydney Ernest, B.Sc.Agr., 42 Telegraph-road, Pymble.
1940		Betty, Robert Cecil, 67 Imperial-avenue, Bondi.
1937	P 6	Birch, Arthur John, M.Sc., D.Phil. ( <i>Oxon.</i> ), 6 Beechcroft-road, Oxford, England.
1916		Birrell, Septimus, 74 Edinburgh-road, Marrickville.
1920		Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale; p.r. 26A Wolseley-road, Mosman.
1939	P 3	Blake, George Gascoigne, M.I.E.E., F.Inst.P., "Holmleigh," Cecil-avenue, Pennant Hills.
1948		Blanks, Fred Roy, B.Sc. (Hons.), Industrial Chemist, 12 Culworth-avenue, Killara.
1946		Blaschke, Ernst Herbert, 6 Illistron Flats, 63 Carrabella-street, Kirribilli.
1933	P 29	Bolliger, Adolph, Ph.D., F.A.C.I., Director of Research, Gordon Craig Urological Research Laboratory, Department of Surgery, University of Sydney. (President, 1945.)
1920	P 9	Booth, Edgar Harold, M.C., D.Sc., F.Inst.P., "Hills and Dales," Mittagong. (President, 1935.)
1939	P 17	Bosworth, Richard Charles Leslie, M.Sc., D.Sc. <i>Adel.</i> , Ph.D. <i>Camb.</i> , F.A.C.I., F.Inst.P., c.o. C.S.R. Co. Ltd., Pyrmont; p.r. 41 Spencer-road, Killara.
1948		Boyd, Eric Harold, B.A., B.Sc., Dip.Ed., F.P.S., The King's School, Parramatta.

## Elected.

- 1948 Boyd, Joan, B.Sc. Hons. *Lond.*, Dip.Ed. *Lond.*, The King's School, Parramatta.
- 1938 Breckenridge, Marion, B.Sc., Department of Geology, The University of Sydney; p.r. 19 Handley-avenue, Thornleigh.
- 1946 Breyer, Bruno, M.D., Ph.D., M.A., F.A.C.I., Lecturer in Agricultural Chemistry, Faculty of Agriculture, University of Sydney, Sydney.
- 1919 P 1 Briggs, George Henry, D.Sc., Ph.D., F.Inst.P., Officer-in-Charge, Section of Physics, National Standards Laboratory of Australia, University Grounds, Sydney; p.r. 13 Findlay-avenue, Roseville.
- 1942 Brown, Desmond J., M.Sc. (*Syd.*), Ph.D. (*Lond.*), D.I.C., Department of Medical Chemistry, Australian National University, 183 Euston-road, London, N.W.1.
- 1935 P 7 Browne, Ida Alison, D.Sc., Senior Lecturer in Palæontology, University of Sydney.
- 1945 Brown, Norma Dorothy (Mrs.), B.Sc., Biochemist, 2 Macauley-street, Leichhardt.
- 1941 Brown, Samuel Raymond, A.C.A. *Aust.*, 87 Ashley-street, Chatswood.
- 1913 P 22 †Browne, William Rowan, D.Sc., Reader in Geology, University of Sydney. (President, 1932.)
- 1947 Buchanan, Gregory Stewart, B.Sc. (Hons.), Lecturer in Physical Chemistry, Sydney Technical College; p.r. 52 Mary-street, Beecroft.
- 1940 Buckley, Lindsay Arthur, B.Sc., 29 Abingdon-road, Roseville.
- 1946 Bullen, Keith Edward, M.A., B.Sc. *N.Z.*, M.A. *Melb.*, Ph.D., Sc.D. *Camb.*, F.R.S., Professor of Applied Mathematics, University of Sydney, Sydney, N.S.W.
- 1898 †Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. *Syd.*, F.R.A.C.S., "Radstocke," Elizabeth Bay.
- 1926 Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.
- 1938 P 2 †Carey, Samuel Warren, D.Sc., Professor of Geology, University of Tasmania, Tasmania.
- 1948 Carroll, Dorothy, B.A., B.Sc., Ph.D., D.I.C., Secretary, Linnean Society of New South Wales, Science House, 157 Gloucester-street, Sydney.
- 1903 P 5 †Carslaw, Horatio Scott, Sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge; Burradoo, N.S.W.
- 1945 Carter, Harold Burnell, B.V.Sc., Research Officer, C.S.I.R., McMaster Laboratory, University Grounds, Sydney.
- 1944 Cavill, George William Kenneth, M.Sc., c/o Department of Organic Chemistry, The University, Liverpool, Great Britain.
- 1913 P 4 †Challinor, Richard Westman, F.R.I.C., A.A.C.I., A.S.T.C., F.C.S.; p.r. 54 Drumalbyn-road, Bellevue Hill. (President, 1933.)
- 1933 Chalmers, Robert Oliver, A.S.T.C., Australian Museum, College Street, Sydney.
- 1940 Chambers, Maxwell Clark, B.Sc., c/o Coty (England) Ltd., 35-41 Hutchinson-street, Moore Park; p.r. 58 Spencer-road, Killara.
- 1913 P 21 †Cheel, Edwin, 40 Queen-street, Ashfield. (President, 1931.)
- 1935 P 2 Churchward, John Gordon, B.Sc.Agr., Ph.D., 1 Hunter-street, Woolwich.
- 1935 Clark, Sir Reginald Marcus, K.B.E., Central Square, Sydney.
- 1938 Clune, Francis Patrick, Author and Accountant, 15 Prince's-avenue, Vaucluse.
- 1941 Cohen, Max Charles, B.Sc., 80 "St. James," Stanley-street, Sydney.
- 1940 Cohen, Samuel Bernard, M.Sc., A.A.C.I., 8 Roseville-avenue, Roseville.
- 1940 P 2 Cole, Edward Ritchie, B.Sc., 7 Wolsten-avenue, Turramurra.
- 1940 P 1 Cole, Joyce Marie, B.Sc., 7 Wolsten-avenue, Turramurra.
- 1948 Cole, Leslie Arthur, Company Executive, 21 Carlisle-street, Rose Bay.
- 1940 Collett, Gordon, B.Sc., 20 Duchess-avenue, Fivedock.
- 1948 Cook, Cyril Lloyd, M.Sc., 176 Ben Boyd-road, Neutral Bay.
- 1946 Cook, Rodney Thomas, A.S.T.C., 10 Riverview-road, Fairfield.
- 1920 Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.
- 1945 Coombes, Arthur Roylance, A.S.T.C. (chem.), 14 Georges River-road, Croydon.
- 1913 P 5 †Coombes, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College; p.r. Bannerman-crescent, Rosebery.
- 1933 Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd., Manufacturing Chemists, Head Office, 379 Kent-street, Sydney.
- 1937 P 8 Cornforth, Rita Harriet, D.Phil. (*Oxon.*), M.Sc. (*Syd.*), c/o Dyson Perrin's Laboratory, South Parks-road, Oxford, England.
- 1940 Cortis-Jones, Beverly, M.Sc., 62 William-street, Roseville.
- 1919 Cotton, Frank Stanley, D.Sc., Research Professor in Physiology in the University of Sydney.

## Elected.

- 1909 P 7 †Cotton, Leo Arthur, M.A., D.Sc., 113 Queen's Parade East, Newport Beach.  
(President, 1929.)
- 1941 P 1 Craig, David Parker, Lecturer in Inorganic Chemistry, University of  
Sydney; p.r. 62 Springdale Rd., Killara.
- 1921 P 1 †Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief  
Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir  
and Meat Works, Homebush Bay; p.r. 101 Villiers-street., Rockdale.
- 1935 P 3 Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.
- 1948 Cymerman, John, Ph.D., D.I.C., A.R.C.S., B.Sc., A.R.I.C., Lecturer in Organic  
Chemistry, University of Sydney.
- 1940 Dadour, Anthony, B.Sc., 25 Elizabeth-street, Waterloo.
- 1890 †Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
- 1919 P 2 de Beuzeville, Wilfred Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.
- 1906 †Dixon, Sir William, "Merridong," Gordon-road, Killara.
- 1913 P 3 †Doherty, William M., F.R.I.C., F.A.C.I., 36 George-street, Marrickville.
- 1928 Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of  
Mines, Sydney; p.r. 18 Hillview-street, Sans Souci.
- 1947 Downes, Alan Marchant, B.Sc. (Hons.), Grandview-avenue, Croydon, Victoria.
- 1948 Doyle, Shirley Kathleen, B.Sc., Microbiologist to H. Jones & Co.; p.r. 74  
Duntroon-avenue, Roseville.
- 1943 Dudgeon, William, Manager, Commonwealth Drug Co., 50-54 Kippax-street,  
Sydney.
- 1937 P 13 Dulhunty, John Allan, D.Sc., Geology Department, University of Sydney;  
p.r. 40 Manning-road, Double Bay. (President, 1947.)
- 1948 Dunlop, Bruce Thomas, B.Sc., Schoolteacher, 77 Stanhope-road, Killara.
- 1924 Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical  
Education and Medical Gymnastics, Manning Building, 449 Pitt-street,  
Sydney; p.r. "Rose Bank," 158 Parramatta-road, Ashfield.
- 1934 P 40 Dwyer, Francis P. J., D.Sc., Lecturer in Chemistry, University of Sydney,  
Sydney.
- 1945 Eade, Ronald Arthur, B.Sc., 21 Steward-street, Leichhardt.
- 1934 P 2 Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University  
of Sydney. (President, 1940.)
- 1940 Emmerton, Henry James, B.Sc., 1 Rosedale-road, Gordon.
- 1937 English, James Roland, L.S., Sydney.
- 1916 P 2 Enright, Walter John, B.A., Solicitor, High-street, West Maitland; p.r. Regent-  
street, West Maitland.
- 1944 Erhart, John Charles, Chemical Engineer, c/o "Ciba" Coy., Basle, Switzerland.
- 1908 †Esdaile, Edward William, 42 Hunter-street, Sydney.
- 1935 Evans, Silvanus Gladstone, A.I.A.A. Lond., A.R.A.I.A., 6 Major-street, Coogee.
- 1944 Fairweather, Alwynne Drysdale (Mrs.), B.Sc., 338 Chapple-street, Broken Hill.
- 1909 P 7 †Fawsitt, Charles Edward, D.Sc., Ph.D., F.A.C.I., Emeritus Professor of  
Chemistry, 14A Darling Point-road, Edgecliff. (President, 1919.)
- 1940 Finch, Franklin Charles, B.Sc., Kirby-street, Rydalmere, N.S.W.
- 1940 Fisher, Robert, B.Sc., 3 Sackville-street, Maroubra.
- 1933 Fletcher, Harold Oswald, Palæontologist, Australian Museum, College-street,  
Sydney.
- 1879 †Foreman, Joseph, M.R.C.S. Eng., L.R.C.P. Edin., "The Astor," Macquarie-street,  
Sydney.
- 1932 Forman, Kenn. P., M.I.Refr.E., 35 Riversdale-road, Hawthorn, Victoria.
- 1905 †Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
- 1940 Franki, Robert James Anning, B.Sc., 891 New South Head-road, Rose Bay.
- 1943 Frederick, Robert Desider Louis, B.E., 162 Buckley-street, Essendon, W.5,  
Victoria.
- 1940 Freney, Martin Raphael, B.Sc., Central Wool Testing House, 17 Randle-street,  
Sydney.
- 1944 P 2 Friend, James Alan, 16 Kelburn-road, Roseville.
- 1945 Furst, Hellmut Friedrich, B.D.S. (Syd.), D.M.D. (Hamburg), Dental Surgeon,  
158 Bellevue-road, Bellevue Hill.
- 1948 Gardiner, Edward Carson, Electrical Engineer in Charge of Construction at the  
Captain Cook Graving Dock, for the Department of Works and Housing  
p.r. 39 Spencer-street, Rose Bay.



## Elected.

1935	P 2	Garretty, Michael Duhan, D.Sc., 477 St. Kilda-road, Melbourne, S.C.2, Victoria.
1939	P 4	Gascoigne, Robert Mortimer, Chemistry Department, University of Liverpool, England.
1926		Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney; p.r. "Wirruna," Belmore-avenue, Wollstonecraft.
1942	P 3	Gibson, Neville Allan, M.Sc., A.R.I.C., Industrial Chemist, 217 Parramatta-road, Haberfield.
1947		Gill, Naida Sugden (Miss), B.Sc., 45 Neville-street, Marrickville.
1947		†Gill, Stuart Frederic, School Teacher, 45 Neville-street, Marrickville.
1940		Gillis, Richard Galvin, Senior Lecturer, Organic Chemistry, Melbourne Technical College; p.r. 4 Tennyson-avenue, Caulfield, S.E.7, Victoria.
1948		Glasson, Kenneth Roderick, B.Sc., Geologist, Lake George Mines Ltd., Captain's Flat, N.S.W.
1945		Goddard, Roy Hamilton, F.C.A. Aust., Royal Exchange, Bridge-street, Sydney.
1947		Goldsworthy, Neil Ernest, M.B., Ch.M. Syd., Ph.D., D.T.M. & H. Camb., D.T.M. & H. Eng., D.P.H. Camb., 65 Roseville-avenue, Roseville.
1936		Goulston, Edna Maude, B.Sc., 83 Birriga-road, Bellevue Hill.
1948		Gray, Charles Alexander Menzies, B.Sc., B.E., 75 Woniara-road, Hurstville.
1938		Griffiths, Edward L., B.Sc., A.A.C.I., A.R.I.C., Chief Chemist, Department of Agriculture; p.r. 151 Wollongong-road, Arncliffe.
1946		Gutmann, Felix, Ph.D., F.Inst.P., M.I.R.E., Commonwealth Research Fellow, Faculty of Agriculture, University of Sydney, Sydney.
1948		Gyarfas, Eleonora Clara, M.Sc. Budapest, Research Assistant, University of Sydney; p.r. 53 Simpson-street, Bondi.
1947		Hall, Lennard Robert, B.Sc., Geological Survey, Department of Mines, Bridge-street, Sydney.
1945		Hall, Leslie Lionel, Works Chemist, 494 Kent-street, Sydney.
1934		Hall, Norman Frederick Blake, M.Sc., Chemist, 15A Wharf-road, Longueville.
1892		†Halloran, Henry Ferdinand, L.S., A.M.I.E.Aust., F.S.I.Eng., M.T.P.I.Eng., 153 Elizabeth-street, Sydney; p.r. 23 March-street, Bellevue Hill.
1940	P 14	Hanlon, Frederick Noel, B.Sc., Geologist, Department of Mines, Sydney.
1905	P 6	†Harker, George, D.Sc., F.A.C.I.; p.r. 89 Homebush-road, Strathfield.
1936		Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., National Standards Laboratory, University Grounds, City-road, Chippendale.
1934		Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo.
1948	P 1	Harris, Clive Melville, Laboratory Assistant, Museum of Technology and Applied Science; p.r. 12 Livingstone-road, Lidcombe.
1946		Harrison, Ernest John Jasper, B.Sc., Geologist, N.S.W. Geological Survey, Department of Mines, Sydney.
1934		Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c.o. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord; p.r. 34 Nicholson-street, Chatswood.
1919		Henriques, Frederick Lester, 208 Clarence-street, Sydney.
1945		Higgs, Alan Charles, Manager, Asbestos Products Pty. Ltd.; p.r. 10 Cremorne-road, Cremorne.
1938	P 4	Hill, Dorothy, M.Sc. Q'ld., Ph.D. Cantab., Geological Research Fellow, University of Queensland, Brisbane.
1946		Hinder, Nora (Miss), B.Sc. Syd., 22 Chester-street, Epping.
1936		Hirst, Edward Eugene, A.M.I.E., Vice-Chairman and Joint Managing Director, British General Electric Co. Ltd.; p.r. "Springmead," Ingleburn.
1928		Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (Aust.), "St. Cloud," Beaconsfield-road, Chatswood.
1948	P 3	Hogarth, Julius William, 8 Jeanneret-avenue, Hunter's Hill.
1916		Hoggan, Henry James, A.M.I.M.E. Lond., A.M.I.E. Aust., Consulting and Designing Engineer, 81 Frederick-street, Rockdale.
1941		Howard, Harold Theodore Clyde, B.Sc., Principal, Technical College, Granville.
1935		Howarth, Mark, F.R.A.S., Grange Mount Observatory, Bull-street, Mayfield, Newcastle, N.S.W.
1938	P 9	Hughes, Gordon Kingsley, B.Sc., Department of Chemistry, University of Sydney, Sydney.
1947		Humpoletz, Justin Ernst, B.Sc. Syd., 21 Belgium-avenue, Roseville.
1923	P 3	†Hynes, Harold John, D.Sc., B.Sc.Agr., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Belbooree," 10 Wandella-avenue, Roseville.

## Elected.

1943		Iredale, Thomas, D.Sc., F.R.I.C., Chemistry Department, University of Sydney, p.r. 96 Roseville-avenue, Roseville.
1942	P 1	Jaeger, John Conrad, M.A., D.Sc., University of Tasmania, Hobart, Tasmania.
1946		Johnson, Guy Frederick, 644 Botany-road, Alexandria.
1909	P 15	Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)
1935	P 6	Joplin, Germaine Anne, B.Sc., Ph.D., Geological Department, University of Sydney; p.r. 18 Wentworth-street, Eastwood.
1948	P 1	Jopling, Alan Victor, B.Sc., B.E., 28 Cliff-street, Manly.
1930		Judd, William Percy, 123 Wollongong-road, Arncliffe.
1935		Kelly, Caroline Tennant (Mrs.), Dip.Anth., "Eight Bells," Cast e Hill.
1940		Kennard, William Walter, 9 Bona Vista-avenue, Maroubra.
1924	P 1	Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 17 Alma-street, Ashfield.
1934		Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial Chemist, 29 Nundah-street, Lane Cove.
1948		Kimble, Frank Oswald, Engineer, 16 Evelyn-avenue, Concord.
1943		Kimble, Jean Annie, B.Sc., Research Chemist, 383 Marrickville-road, Marrickville.
1920		Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo; p.r. 18 Lyne-road, Cheltenham.
1948		Knight, Oscar Le Maistre, B.E. Syd., A.M.I.C.E., A.M.I.E.Anst., Engineer, 10 Mildura-street, Killara.
1948		Koch, Leo E., Ph.D., D.Sc. (Cologne), Department of Geology, The University of Sydney.
1939	P 1	Lambeth, Arthur James, B.Sc., "Naranje," Sweethaven-road, Wetherill Park, N.S.W.
1936		Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., British Australian Lead Manufacturers Pty. Ltd., Box 21, P.O., Concord.
1946		Lederer, Michael, 67 Edgecliff-road, Bondi Junction.
1947		Le Fevre, Raymond James Wood, D.Sc., Ph.D., F.R.I.C., Professor of Chemistry, Chemistry Department, University of Sydney, Sydney.
1936	P 2	Lemberg, Max Rudolph, D.Phil., Institute of Medical Research, Royal North Shore Hospital, St. Leonards.
1920		Le Souef, Albert Sherbourne, 3 Silex-road, Mosman.
1929	P 56	†Lions, Francis, B.Sc., Ph.D., A.R.I.C., Reader, Department of Chemistry, University of Sydney. (President, 1946-47.)
1942		Lippmann, Arthur S., M.D., 175 Macquarie-street, Sydney.
1947		Lloyd, James Charles, B.Sc. Syd., N.S.W. Geological Survey, 41 Goulburn-street, Liverpool.
1940	P 1	Lockwood, William Hutton, B.Sc., F. & A. Inspectorate, 64 H.Q., C.C.G., Minden, Germany.
1906		†Loney, Charles Augustus Luxton, M.Am.soc.Refr.E., National Mutual Building, 350 George-street, Sydney.
1947		Lowenbein, Gladys Olive (Mrs.), B.Sc. Melb., F.R.I.C. Gt. B., A.A.C.I., Director of Research, Australian Leather Research Association; p.r. "Cahors," No. 75, 117 Macleay-street, Potts Point.
1943		†Luber, Daphne (Mrs.), B.Sc., 98 Lang-road, Centennial Park.
1945		Luber, Leonard, Pharmacist, 80 Queen-street, Woollahra.
1948		Lyons, Lawrence Ernest, B.A., M.Sc., Lecturer in Chemistry, The University of Sydney; p.r. 13 Albert-road, Strathfield.
1942		Lyons, Raymond Norman Matthew, M.Sc., Biochemical Research Worker, 84 Marine-parade, Maroubra.
1939	P 4	Maccoll, Allan, M.Sc., Department of Chemistry, University College, Gower-street, London, W.C.1.
1943		McCoy, William Kevin, Analytical Chemist, c/o Mr. A. J. McCoy, 39 Malvern-avenue, Merrylands.
1940		McGrath, Brian James, 40 Mooramie-avenue, Kensington.
1940		McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills.
1948		McInnes, Gordon Elliott, Department of Geology, The University of Sydney; p.r. 46 Laycock-street, Bexley.

## Elected.

1906	P 2	†McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville.
1891	P 1	†McKay, R. T., M.Inst.C.E., Eldon Chambers, 92 Pitt-street, Sydney.
1944	P 7	McKenzie, Hugh Albert, B.Sc., c/o Frick Chemical Laboratory, Princeton University, Princeton, New Jersey, U.S.A.
1943		McKern, Howard Hamlet Gordon, A.S.T.C., A.A.C.I., Assistant Chemist, Museum of Technology and Applied Science, Harris-street, Ultimo; p.r. Flat 2, 42A, Waimea-street, Burwood.
1947		McMahon, Patrick Reginald, M.Agr.Sc. N.Z., Ph.D. Leeds, A.R.I.C., A.N.Z.I.C., Lecturer-in-charge, Sheep and Wool Department, Sydney Technical College, East Sydney.
1927		McMaster, Sir Frederick Duncan, kt., "Dalkeith," Cassilis, N.S.W.
1943		McNamara, Barbara Joyce (Mrs.), M.B., B.S., Yeoval, 7.W.
1946		McPherson, John Charters, 14 Sarnar-road, Greenwich.
1946	P 1	McRoberts, Helen May, B.Sc., New England University College, Armidale.
1947		Magee, Charles Joseph, D.Sc.Agr. Syd., M.Sc. Wis., Chief Biologist, Department of Agriculture; p.r. 4 Alexander-parade, Roseville.
1947		Maley, Leo Edmund, M.Sc., B.Sc. (Hons.), A.A.C.I., A.M.A.I.M.M., 116 Maitland road, Mayfield.
1940		Malone, Edward E., 33 Windsor-road, St. Mary's.
1947	P 8	Mapstone, George E., M.Sc., A.A.C.I., M.Inst.Pet., Chief Chemist of National Oil Pty. Ltd., Glen Davis; p.r. 2 Anderson Square, Glen Davis, N.S.W.
1944		Martin, Cyril Maxwell, Chemist, 22 Wattle-street, Haberfield.
1946		May, Albert, Ph.D., M.A., 94 Birriga-road, Bellevue Hill.
1935	P 1	Maze, Wilson Harold, M.Sc., Deputy Registrar, University of Sydney, Sydney.
1912		†Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Manly.
1929	P 25	Mellor, David Paver, D.Sc., F.A.C.I., Reader, Department of Chemistry, University of Sydney; p.r. 137 Middle Harbour-road, Lindfield. (President, 1941-42.)
1941		Melville, George Livingstone, Managing Director, Federal Machine Co. Ltd., Loftus-street, Arncliffe.
1928		Micheli, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, "Walla Walla," Hull-road, Beecroft.
1940		Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd. 15 Shaw-avenue, Earlwood.
1941		Morrissey, Matthew John, B.A., A.S.T.C., Auburn-street, Parramatta.
1922	P 28	Morrison, Frank Richard, A.A.C.I., F.C.S., Deputy Director, Museum of Technology and Applied Science, Harris-street, Ultimo.
1934		Mort, Francis George Arnot, A.A.C.I., Chemist, 16 Grafton-street, Woollahra.
1948		Mosher, Kenneth George, B.Sc., Geologist, Geological Survey, Department of Mines, Bridge-street, Sydney.
1944		Moye, Daniel George, B.Sc., Geologist, Warragamba Dam.
1946		Mulholland, Charles St. John, B.Sc., Geologist, Department of Mines, Sydney.
1948		Mulley, Joan W., Technical Officer, C.S.I.R.; p.r. 4 Billyard-avenue, Elizabeth Bay.
1915		Murphy, Robert Kenneth, Dr.Eng., Chem., A.S.T.C., M.I.Chem.E., F.A.C.I., Principal, Sydney Technical College, Sydney.
1923	P 2	Murray, Colonel Jack Keith, B.A., B.Sc.Agr., Administrator, Territory of Papua-New Guinea, Government House, Port Moresby.
1948		Naylor, Betty Yvonne, B.Sc., 6 Niblick-avenue, Roseville.
1930	P 6	Naylor, George Francis King, M.A., M.Sc., Dip.Ed., A.A.I.I.P., Lecturer in Philosophy and Psychology, University of Queensland, Brisbane, Qld.
1943		Neuhaus, John William George, 190 Old Prospect-road, Wentworthville.
1932		Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Professor of Botany, The University of Ceylon, Colombo, Ceylon.
1943		Nicol, Alexander Campbell, A.S.T.C., A.A.C.I., Chief Chemist, Crown Crystal Glass Co.; p.r. No. 2 Flat, corner Hendy-avenue and Rainbow-streets, Coogee.
1935		Nicol, Phyllis Mary, M.Sc., Sub-Principal, The Women's College, Newtown.
1945	P 1	Noakes, Lyndon Charles, Geologist, c/o Mineral Resources Survey, Canberra, A.C.T.
1938	P 1	Noble, Norman Scott, D.Sc.Agr., M.Sc., D.I.C., c/o C.S.I.R., 314 Albert-street, East Melbourne, Vic.
1920	P 4	†Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Under Secretary, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road, Lindfield. (President, 1934.)

## Elected.

1947		Nordon, Peter, A.S.T.C., A.A.C.I., Chemical Engineer, 1 Edgecliff-road, Bondi Junction.
1948		Northcott, Jean, B.Sc. (Hons.), Chemistry Department, The University of Sydney; p.r. 38 Canberra-street, Lane Cove.
1940	P 25	Nyholm, Ronald Sydney, M.Sc., Chemistry Department, University College, Gower-street, London, W.C.1, England.
1935	P 4	O'Connell, Rev. Daniel J. K., S.J., M.Sc., D.Ph., F.R.A.S., Riverview College Observatory, Sydney.
1947		Old, Adrian Noel, B.Sc.Agr., Chemist, Department of Agriculture; p.r. 4 Springfield-avenue, Pott's Point.
1921	P 10	Osborne, George Davenport, D.Sc. <i>Syd.</i> , Ph.D. <i>Camb.</i> , Senior Lecturer in Geology in the University of Sydney. (President, 1944.)
1920	P 75	Penfold, Arthur Ramon, F.A.C.I., F.C.S., Director, Museum of Technology and Applied Science, Harris-street, Ultimo. (President, 1931.)
1948		Perry, Hubert Roy, B.Sc., 74 Woodbine-street, Bowral.
1938		Phillips, Marie Elizabeth, B.Sc., 4 Morella-road, Clifton Gardens.
1935		Phillips, Orwell, 55 Darling Point-road, Edgecliff.
1946		Pinwell, Norman, B.A. ( <i>Q'land</i> ), The Scots College, Bellevue Hill.
1943		Plowman, Ronald Arthur, A.S.T.C., A.A.C.I., Analytical Chemist, 78 Alt-street, Ashfield.
1919		Poate, Hugh Raymond Guy, M.B., Ch.M. <i>Syd.</i> , F.R.C.S. <i>Eng.</i> , L.R.C.P. <i>Lond.</i> , F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellevue Hill.
1896		†Pope, Roland James, B.A. <i>Syd.</i> , M.D., Ch.M., F.R.C.S. <i>Edin.</i> , 185 Macquarie-street, Sydney.
1946		Potter, Bryce Harrison, B.Sc. (Hons.) ( <i>Syd.</i> ), 13 Fuller's-road, Chatswood.
1921	P 2	Powell, Charles Wilfrid Roberts, F.R.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman.
1938		Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern.
1945		Prescott, Alwyn Walker, B.Eng., Lecturer in Mechanical and Electrical Engineering in the University of Sydney; p.r. Harris-road, Normanhurst.
1927		Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 8 Wattle-street, Killara.
1918	P 1	Priestley, Henry, M.D., Ch.M., B.Sc., Professor of Biochemistry, Faculty of Medicine, the University of Sydney. (President, 1942-43.)
1945		Proud, John Seymour, Mining Engineer, 4 View-street, Chatswood.
1893		†Purser, Cecil, B.A., M.B., Ch.M. <i>Syd.</i> , "Ascot," Grosvenor-road, Wahroonga.
1935	P 3	†Quodling, Florrie Mabel, B.Sc., Lecturer in Geology, University of Sydney
1922	P 6	Raggatt, Harold George, D.Sc., Director, Mineral Resources Survey, Department of Supply, Canberra, A.C.T.
1940	P 2	Ralph, Colin Sydney, B.Sc., 24 Canberra-street, Epping.
1919	P 3	Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., 57 William-street, Sydney.
1936		Randall, Harry, Buena Vista-avenue, Denistone.
1947		Ray, Nancy Evelyn (Mrs.), Plastics Manufacturer, 14 Hedger-avenue, Ashfield.
1947		Ray, Reginald John, Plastics Manufacturer and Research Chemist, 14 Hedger-avenue, Ashfield.
1931	P 1	Rayner, Jack Maxwell, B.Sc., F.Inst.P., Chief Geophysicist, Bureau of Mineral Resources, Geology and Geophysics, 485 Bourke-street, Melbourne, Vic.
1935		Reid, Cicero Augustus, 19 Newton-road, Strathfield.
1947		Reuter, Fritz Henry, Ph.D. ( <i>Berlin</i> , 1930), F.A.C.I., 94 Onslow-street, Rose Bay.
1946		Rhodes-Smith, Cecil, 261 George-street, Sydney.
1947		Ritchie, Arthur Sinclair, A.S.T.C., Lecturer in Mineralogy and Geology, New-castle Technical College; p.r. 188 St. James-road, New Lambton, N.S.W.
1947		Ritchie, Bruce, B.Sc. (Hons.), c/o Pyco Products Pty. Ltd., 576 Parramatta-road, Petersham.
1939	P 16	Ritchie, Ernest, M.Sc., Senior Lecturer, Chemistry Department, University of Sydney, Sydney.
1939	P 3	Robbins, Elizabeth Marie (Mrs.), M.Sc., 344 Railway-parade, Guildford.

## Elected.

1933		Roberts, Richard George Crafter, Electrical Engineer, c/o C. W. Stirling & Co., Asbestos House, York and Barrack-streets, Sydney.
1940		Robertson, Rutherford Ness, B.Sc. <i>Syd.</i> , Ph.D. <i>Cantab.</i> , Senior Plant Physiologist, C.S.I.R., Division of Food Preservation, Private Bag, P.O., Homebush ; p.r. Flat 4, 43 Johnston-street, Annandale.
1935	P 2	Room, Thomas G., M.A., F.R.S., Professor of Mathematics in the University of Sydney.
1940		Rosenbaum, Sidney, 44 Gilderthorp-avenue, Randwick.
1948		Rosenthal-Schneider, Ilse, Ph.D., 48 Cambridge-avenue, Vaucluse.
1940		Ross, Jean Elizabeth, B.Sc., Dip.Ed., 5 Stanton-road, Haberfield.
1948		Ross, Leonard Paul, B.Sc., 137 Burwood-road, Enfield.
1945		Rountree, Phyllis Margaret, M.Sc. <i>Melb.</i> , Dip.Bact. <i>Lond.</i> , Royal Prince Alfred Hospital, Sydney.
1945		Sambell, Pauline Mary, B.A. (Zoology), Assistant Research Officer, McMaster Laboratory ; p.r. 83 Woniora-road, Hurstville.
1945		Sampson, Aileen (Mrs.), sc.Dip. (A.S.T.C., 1944), 9 Knox-avenue, Epping.
1941	P 3	Sawkins, Dansie Thomas, M.A. <i>Syd.</i> , B.A. <i>Camb.</i> , 60 Boundary-street, Roseville.
1920		Scammell, Rupert Boswood, B.Sc. <i>Syd.</i> , A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern ; p.r. 10 Buena Vista-avenue, Clifton Gardens.
1948	P 1	Schafer, Harry Neil Scott, B.Sc., 18 Bartlett-street, Summer Hill.
1946	P 1	Scott, Beryl (Miss), B.Sc., Geology Department, University of Tasmania.
1940		Scott, Reginald Henry, B.Sc., 3 Walbundry-avenue, East Kew, Victoria.
1933		Selby, Esmond Jacob, Dip.Com., Sales Manager, Box 175 D, G.P.O., Sydney.
1936		Sellenger, Brother Albertus, St. Ildephonsus College, New Norcia, W.A.
1948		Sharp, Kenneth Raeburn, Geology Department, The University of Sydney ; p.r. Kitchener-road, St. Ives.
1938		Sheahan, Thomas Henry Kennedy, B.Sc., Chemist, c/o Shell Co. of Aust., North Terrace, Adelaide.
1936	P 2	Sherrard, Kathleen Margaret Maria (Mrs.), M.Sc. <i>Melb.</i> , 43 Robertson-road, Centennial Park.
1948		Sherwood, Ian Russell, D.Sc., F.A.C.I., Research Bacteriologist, Research Laboratory, Colonial Sugar Refining Co. Ltd., John-street, Pyrmont.
1945		Shulman, Albert, B.Sc., Industrial Chemist, Flat 2, Linden Court, Linden-avenue, Woollahra.
1945	P 2	Simmons, Lewis Michael, B.Sc. (Hons.) <i>Lond.</i> , Ph.D. <i>Lond.</i> , F.A.C.I., Head of Science Department, Scots College ; p.r. The Scots College, Victoria-road, Bellevue Hill.
1948		Simonett, David Stanley, B.Sc., Geography Department, The University of Sydney ; p.r. 14 Selwyn-street, Artarmon.
1943		Simpson, John Kenneth Moore, Industrial Chemist, "Browie," Old Castle Hill-road, Castle Hill.
1933		Slade, George Hermon, B.Sc., Director, W. Hermon Slade & Co. Pty. Ltd., Manufacturing Chemists, Mandemur-avenue, Homebush ; p.r. "Raiaatea," Oyama-avenue, Manly.
1940		Smith, Eric Brian Jeffcoat, New College, Oxford, England.
1947		Smith-White, William Broderick, M.A. <i>Cantab.</i> , B.Sc. <i>Syd.</i> , Department of Mathematics, University of Sydney ; p.r. 7 Henson-street, Summer Hill.
1919		Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
1921		Spencer-Watts, Arthur, "Araboono," Glebe-street, Randwick.
1916		Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.
1914		†Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney ; p.r. Captain Piper's-road and New South Head-road, Vaucluse.
1948	P 1	Stevens, Neville Cecil, B.Sc., Geology Department, The University of Sydney ; p.r. 12 Salisbury-street, Hurstville.
1900	P 1	†Stewart, J. Douglas, B.V.Sc., F.R.C.V.S., Emeritus Professor of Veterinary Science in the University of Sydney ; p.r. "Berelle," Homebush-road, Strathfield. (President, 1927.)
1942		Still, Jack Leslie, B.Sc., Ph.D., Department of Biochemistry, The University, Sydney.
1916	P 1	Stone, Walter George, F.S.T.C., F.A.C.I., Chief Analyst, Department of Mines, Sydney ; p.r. 79 Ocean-street, Woollahra.
1918		†Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes ; Box 23, P.O., Burwood ; p.r. "Stonycroft," 10 Redmyre-road, Strathfield.



## Elected.

1919		†Sutherland, George Fife, A.R.C.Sc. <i>Lond.</i> , Assistant Professor of Mechanical Engineering in the University of Sydney.
1920		Sutton, Harvey, O.B.E., M.D., D.P.H. <i>Melb.</i> , B.Sc. <i>Oxon.</i> , Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney; p.r. "Lynton," 27 Kent-road, Rose Bay.
1941	P 2	Swanson, Thomas Baikie, M.Sc. <i>Adel.</i> , c/o Technical Service Department, Icianz, Box 1911, G.P.O., Melbourne, Victoria.
1948		Swinbourne, Ellice Simmons, Organic Chemist, 183 Sydney-road, Balgowlah.
1915	P 3	Taylor, Brigadier Harold B., M.C., D.Sc., F.R.I.C., F.A.C.I., Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney; p.r. 44 Kenneth-street, Longueville.
1944		Thomas, Andrew David, Squadron Leader, R.A.A.F., M.Sc., A.Inst.P., 17 Millicent-avenue, Toorak, Melbourne, E.2., Vic.
1946		Thomas, Ifor Morris, M.Sc., Department of Zoology, University of Adelaide, Adelaide, S.A.
1919		Thorne, Harold Henry, M.A. <i>Cantab.</i> , B.Sc. <i>Syd.</i> , F.R.A.S., Lecturer in Mathematics in the University of Sydney; p.r. 55 Railway-crescent, Beecroft.
1935		Tommerup, Eric Christian, M.Sc., A.A.C.I., Queensland Agricultural College, Lawes, via Brisbane, Queensland.
1923		Toppin, Richmond Douglas, A.R.I.C., 51 Crystal-street, Petersham.
1940		Tow, Aubrey James, M.Sc., No. 5, "Werrington," Manion-avenue, Rose Bay.
1943		Turner, Ivan Stewart, M.A., M.Sc., Ph.D., Lecturer in Mathematics, University of Sydney; p.r. 120 Awaba-street, Mosman.
1921		Vicars, Robert, Marrickville Woollen Mills, Marrickville.
1935		Vickery, Joyce Winifred, M.Sc., Botanic Gardens, Sydney; p.r. 17 The Promenade, Cheltenham.
1933	P 5	Voisey, Alan Heywood, D.Sc., Lecturer in Geology and Geography, New England University College, Armidale.
1903	P 10	†Vonwiller, Oscar U., B.Sc., F.Inst.P., Emeritus Professor of Physics in the University of Sydney; p.r. "Eightbells," Old Castle Hill-road, Castle Hill. (President, 1930.)
1948		Walker, Donald Francis, Surveyor, 13 Beauchamp-avenue, Chatswood.
1943		Walker, James Foote, Company Secretary, 11 Bruce-avenue, Epping.
1919	P 2	Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney; p.r. 45 Nelson-road, Killara. (Member from 1910-1913. President, 1943-44.)
1913	P 5	†Wardlaw, Hy. Sloane Halero, D.Sc. <i>Syd.</i> , F.A.C.I., Lecturer and Demonstrator in Biochemistry in the University of Sydney. (President, 1939.)
1944		Warner, Harry, A.S.T.C., Chemist, 6 Knibbs-street, Turner, Canberra, A.C.T.
1921		†Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., c/o Mrs. Millett, Illoura-avenue, Wahroonga.
1919	P 1	Waterhouse, Lionel Lawry, B.E. <i>Syd.</i> , Reader in Geology in the University of Sydney.
1919	P 7	Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Research Professor of Agriculture, University of Sydney; p.r. "Hazelmere," Chelmsford-avenue, Lindfield. (President, 1937.)
1944		Watkins, William Hamilton, B.Sc., Industrial Chemist, 57 Bellevue-street, North Sydney.
1911	P 1	†Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney; p.r. 64 Wentworth-road, Vaucluse. (President, 1925.)
1947		Webb, Gordon Keyes, A.F.I.A., A.C.I.S., Accountant, c/o Max Wurcker (1930) Pty. Ltd., 99 York-street, Sydney.
1921		Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney.
1947		Werner, Ronald Louis, Industrial Chemist, 25 Dine-street, Randwick.
1946		Weston, Margaret Crowley, B.A., 41 Bulkara-road, Bellevue Hill.
1909	P 3	†White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, University Grounds, Newtown.
1943		Whiteman, Reginald John Nelson, M.B., Ch.M., F.R.A.C.S., 143 Macquarie-street, Sydney.
1928		Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, Bram Hall, Jersey-road, Strathfield.
1942		Williams, Gordon Roy, B.Sc., 45 Conder-street, Burwood.

## Elected.

1945		Willis, Jack Lehane, B.Sc., Flat 5, "Narooma", Hampden-street, North Sydney.
1943		Winch, Leonard, B.Sc., 60 Baldwin-avenue, Asquith.
1940		Wogan, Samuel James, Range-road, Sarina, North Queensland.
1936	P 7	Wood, Harley Weston, M.Sc., A.Inst.P., F.R.A.S., Government Astronomer, Sydney Observatory, Sydney.
1906	P 12	†Woolnough, Walter George, D.Sc., F.G.S., c/o Mr. W. L. Woolnough, "Callabonna", 8 Park-avenue, Gordon.
1916		Wright, George, Company Director, c/o Hector Allen, Son & Morrison, 7 Wynyard-street, Sydney.
1946		Wyndham, Norman Richard, M.D., M.S. ( <i>Syd.</i> ), F.R.C.S. ( <i>Eng.</i> ), F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney.
1948		Zingel, Judith, B.Sc., Geology Department, The University of Sydney; p.r. 89 Sydney-road, Manly.

## HONORARY MEMBERS.

*Limited to Twenty.*

## Elected.

1949		Burnet, Frank Macfarlane, M.D., Ph.D., F.R.S., Director of the Walter and Eliza Hall Research Institute, Melbourne.
1949		Florey, Sir Howard, M.B., B.S., B.Sc., M.A., Ph.D., F.R.S., Professor of Pathology, Oxford University, England.
1914		Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England.
1946		Jones, Sir Harold Spencer, M.A., D.Sc., F.R.S., Astronomer Royal, Royal Observatory, Greenwich, London, S.E.10.
1915		Maitland, Andrew Gibb, F.G.S., "Bon Accord," 28 Melville-terrace, South Perth, W.A.
1912		Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England.
1948		Oliphant, Marcus L., B.Sc., Ph.D., F.R.S., Professor of Physics, The University, Edgbaston, Birmingham 15, England.
1948		Robinson, Sir Robert, M.A., D.Sc., F.C.S., F.I.C., F.R.S., Professor of Chemistry, Oxford University, England.
1946		Wood-Jones, F., D.Sc., M.B., B.S., F.R.C.S., L.R.C.P. ( <i>Lond.</i> ), F.R.S., F.Z.S., Professor of Anatomy, University of Manchester, England.

## OBITUARY, 1948-49.

1909	Ernest Clayton Andrews.
1923	George Frederick Birks.
1932	Ernest Norman McKie.
1920	Edward Montague Wellish.

## THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke "as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

### CLARKE MEMORIAL LECTURES.

#### Delivered.

1906. "The Volcanoes of Victoria," and "The Origin of Dolomite" (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.
1907. "Geography of Australia in the Permo-Carboniferous Period" (two lectures). By Professor T. W. E. David, B.A., F.R.S.
- "The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.
- "Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.
- "The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.
1918. "Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.
1919. "Geology at the Western Front," By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.
1936. "The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (THIS JOURN., 1936, 70, 39.)
1937. "Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (THIS JOURN., 1937, 71, 68.)
1938. "The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E., D.Sc. (Oxon.). (THIS JOURN., 1938, 71, 503.)
1939. "Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S. (THIS JOURN., 1939, 73, 41.)
1940. "The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (THIS JOURN., 1940, 74, 283.)
1941. "The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (THIS JOURN., 1941, 75, 47.)
1942. "The Heroic Period of Geological Work in Australia." By E. C. Andrews, B.Sc.
1943. "Australia's Mineral Industry in the Present War." By H. G. Raggatt, D.Sc.
1944. "An Australian Geologist Looks at the Pacific." By W. H. Bryan, M.C., D.Sc.
1945. "Some Aspects of the Tectonics of Australia." By Professor E. S. Hills, D.Sc., Ph.D.
1946. "The Pulse of the Pacific." By Professor L. A. Cotton, M.A., D.Sc.
1947. "The Teachers of Geology in Australian Universities." By Professor H. S. Summers, D.Sc.
1948. "The Sedimentary Succession of the Bibliando Dome : Record of a Prolonger Proterozoic Ice Age." By Sir Douglas Mawson, O.B.E., F.R.S., D.Sc., B.E.

### AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

*Vice-President from 1866 to 1878.*

The prefix \* indicates the decease of the recipient.

#### Awarded.

- 1878 \*Professor Sir Richard Owen, K.C.B., F.R.S.
- 1879 \*George Bentham, C.M.G., F.R.S.
- 1880 \*Professor Thos. Huxley, F.R.S.
- 1881 \*Professor F. M'Coy, F.R.S., F.G.S.
- 1882 \*Professor James Dwight Dana, LL.D.
- 1883 \*Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
- 1884 \*Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.

## Awarded.

- 1885 \*Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.  
 1886 \*Professor L. G. De Koninck, M.D.  
 1887 \*Sir James Hector, K.C.M.G., M.D., F.R.S.  
 1888 \*Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.  
 1889 \*Robert Lewis John Ellery, F.R.S., F.R.A.S.  
 1890 \*George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.  
 1891 \*Captain Frederick Wollaston Hutton, F.R.S., F.G.S.  
 1892 \*Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.  
 1893 \*Professor Ralph Tate, F.L.S., F.G.S.  
 1895 \*Robert Logan Jack, LL.D., F.G.S., F.R.G.S.  
 1895 \*Robert Etheridge, Jnr.  
 1896 \*The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.  
 1900 \*Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.  
 1901 \*Edward John Eyre.  
 1902 \*F. Manson Bailey, C.M.G., F.L.S.  
 1903 \*Alfred William Howitt, D.Sc., F.G.S.  
 1907 \*Professor Walter Howchin, F.G.S., University of Adelaide.  
 1909 \*Dr. Walter E. Roth, B.A.  
 1912 \*W. H. Twelvvetrees, F.G.S.  
 1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.  
 1915 \*Professor W. A. Haswell, M.A., D.Sc., F.R.S.  
 1917 \*Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., Sc.D., D.Sc., F.R.S., F.G.S.  
 1918 \*Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.  
 1920 \*Joseph Edmund Carne, F.G.S.  
 1921 \*Joseph James Fletcher, M.A., B.Sc.  
 1922 \*Richard Thomas Baker, The Crescent, Cheltenham.  
 1923 \*Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.  
 1924 \*Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.  
 1925 \*Charles Hedley, F.L.S.  
 1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.  
 1928 Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.  
 1929 Professor Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.  
 1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.  
 1931 \*Robin John Tillyard, M.A., D.Sc., Sc.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.  
 1932 \*Frederick Chapman, A.L.S., F.R.S.N.Z., F.G.S., Melbourne.  
 1933 Walter George Woolnough, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.  
 1934 \*Edward Sydney Simpson, D.Sc., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.  
 1935 \*George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.  
 1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E., University of Adelaide.  
 1937 J. T. Jutson, B.Sc., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.  
 1938 \*Professor H. C. Richards, D.Sc., The University of Queensland, Brisbane.  
 1939 \*C. A. Sussmiltch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.  
 1941 Professor Frederic Wood Jones, M.B., B.S., D.Sc., F.R.S., Anatomy Department, University of Manchester, England.  
 1942 William Rowan Browne, D.Sc., Reader in Geology, The University of Sydney, N.S.W.  
 1943 Walter Lawry Waterhouse, M.C., D.Sc.Agric., D.I.C., F.L.S., Reader in Agriculture, University of Sydney.  
 1944 Professor Wilfred Eade Agar, O.B.E., M.A., D.Sc., F.R.S., University of Melbourne, Carlton, Victoria.  
 1945 Professor William Noel Benson, B.A., D.Sc., F.G.S., F.R.G.S., F.R.S.N.Z., F.G.S.A.M., University of Otago, Dunedin, N.Z.  
 1946 Black, J. M., A.L.S. (*honoris causa*), Adelaide, S.A.  
 1947 \*Hubert Lyman Clark, A.B. D.Sc., Ph.D., Hancock Foundation, U.S.C., Los Angeles, California.  
 1948 Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney.

## AWARDS OF THE JAMES COOK MEDAL.

*Bronze Medal.*

Awarded annually for outstanding contributions to science and human welfare in and for the Southern Hemisphere.

- 1947 Smuts, Field-Marshal The Rt. Hon. J. C., P.C., C.H., K.C., D.T.D., LL.D., F.R.S., Chancellor, University of Capetown, South Africa.  
 1948 Houssay, Bernardo A., Professor of Physiology, Instituto de Biología y Medicina Experimental, Buenos Aires, Argentina.

## AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

*Money Prize of £25.*

## Awarded.

- 1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."
- 1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

*The Society's Bronze Medal.*

- 1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."
- 1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."
- 1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."
- 1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."
- 1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."
- 1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."
- 1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."
- 1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."
- 1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."
- 1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."
- 1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."
- 1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."
- 1943 Edwin Cheel, Sydney, in recognition of his contributions in the field of botanical research and to the advancement of science in general.
- 1948 Waterhouse, Walter L., M.S., D.Sc.Agr., D.I.C., F.L.S., Sydney, in recognition of his valuable contributions in the field of agricultural research.

## AWARDS OF THE WALTER BURFITT PRIZE.

*Bronze Medal and Money Prize of £75.*


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Established as the result of a generous gift to the Society by Dr. W. F. BURFITT, B.A., M.B., Ch.M., B.Sc., of Sydney, which was augmented later by a gift from Mrs. W. F. BURFITT. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past six years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

## Awarded.

- 1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.
- 1932 Charles Hallibly Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
- 1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.
- 1938 Frank Macfarlane Burnet, M.D. (*Melb.*), Ph.D. (*Lond.*), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
- 1941 Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.
- 1944 Hereward Leighton Kesteven, D.Sc., M.D., c/o Allied Works Council, Melbourne.
- 1947 John Conrad Jaeger, M.A., D.Sc., University of Tasmania, Hobart.
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## AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (THIS JOURNAL, Vol. LXII, pp. x-xiii, 1928.)

**Awarded.**

- 1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.
- 1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.
- 1940 G. J. Burrows, B.Sc., University of Sydney.
- 1942 J. S. Anderson, B.Sc., Ph.D. (Lond.), A.R.C.S., D.I.C., University of Melbourne.
- 1944 F. P. Bowden, Ph.D., Sc.D., University of Cambridge, Cambridge, England.
- 1946 Briggs, L. H., D.Phil. (Oxon.), D.Sc. (N.Z.), F.N.Z.I.C., F.R.S.N.Z., Auckland University College, Auckland, N.Z.
- 1948 Ian Lauder, M.Sc., Ph.D., University of Queensland, Brisbane.

# Royal Society of New South Wales

REPORT OF THE COUNCIL FOR THE YEAR ENDING 31st MARCH, 1949.

PRESENTED AT THE ANNUAL GENERAL MEETING OF THE SOCIETY, 6th APRIL, 1949

(RULE XXVI).

The membership of the Society at the end of the period under review stood at 354. Thirty-eight new members were elected during the year, the Council having made a special effort towards increased enrolment; however, twelve members were lost by resignation and four, who were in arrears with subscriptions, were removed from the register. Four members have been lost to the Society by death since 1st April, 1948:

Ernest Clayton Andrews (1909).

George Frederick Birks (1923).

Ernest Norman McKie (1932).

Edward Montague Wellish (1920).

Professor Marcus L. Oliphant, B.Sc., Ph.D., F.R.S., and Professor Sir Robert Robinson, M.A., D.Sc., F.C.S., F.I.C., F.R.S., were elected to honorary membership of the Society at the annual meeting on 7th April, 1948.

During the year nine general monthly meetings were held, at which the average attendance was 49. Thirty-nine papers were accepted for reading and publication by the Society, an increase of four from the previous year.

At the annual and general monthly meeting of 7th April, 1948, the Acting President, Dr. F. Lions, welcomed Professor Griffith Taylor, of the University of Toronto, Canada, formerly of Sydney University. Professor Taylor gave an address describing the application of geography, geology and physiography to national planning.

The Council decided to devote portion of the time of general meetings to "Notes, Exhibits and Questions". This seems to have met with success, and the following questions have been answered:

4th August:

"There is evidence that ice ages have occurred simultaneously in both hemispheres of the world—what is the evidence of this?" Answered by Dr. G. D. Osborne.

"What is a Transcendental Number?" Answered by Mr. W. B. Smith-White.

"What are Cosmic Rays?" Answered by Dr. R. E. B. Makinson.

6th October:

"Why are there black and white races?" Answered by Professor A. P. Elkin.

"Why does the moon always turn the same face towards the earth?" Answered by Mr. Harley Wood.

1st December:

"What is the principle of the electron microscope?" Answered by Mr. R. L. Werner.

"What was the cause of the change of longitude of Sydney Observatory amounting to some 166 yards in about the year 1932, as indicated by certain one-inch military maps?" Answered by Mr. Harley Wood.

Exhibits discussed were:

5th May:

"Bouncing Putty", by Dr. D. P. Mellor.

3rd June:

"Enlarged photographs of the Second Positive Spectrum of Nitrogen, showing some features of interest", by Professor O. U. Vonwiller and Miss D. P. Tarrant.

A symposium on the "Education of a Scientist" was held at the general monthly meeting on 1st September, the following addresses being given:

- "Science in Secondary Education", by Mr. J. B. Thornton.
- "The Teaching of Science in the Universities", by Professor N. A. Burges.
- "The Scientist and Scientific Method", by Professor K. E. Bullen.

The topic stimulated a deal of discussion, which was continued by other speakers at the next general meeting.

Addresses commemorating great scientists and important scientific events were given at the general monthly meeting on 3rd November:

- "Simon Stevin" (Stevinus), by Mr. H. H. Thorne.
- "Berzelius", by Mr. J. B. Thornton.
- "Important Events in the History of Public Health", by Professor Harvey Sutton.

In continuance of its programme of popular education as to atomic energy, the Society made arrangements with the University Extension Board for the delivery of a series of lectures on atomic physics during July:

- "The Atom and Radioactivity", by Dr. D. P. Mellor.
- "Artificial Transformations and Nuclear Fission", by Dr. R. E. B. Makinson.
- "Atomic Physics and Human Welfare", by Dr. F. Lions.
- "International Control of Atomic Energy", by Dr. G. H. Briggs.

Four Popular Science Lectures were delivered during the year, and much appreciated by members of the Society and the public:

- 20th May: "The Struggle between Fungi and Roots", by Professor N. A. Burges.
- 17th June: "Plant Growth Regulators or Hormones", by Dr. C. J. Magee.
- 16th September: "The Making of an Australian—A Study in Migration", by Mrs. C. Kelly.
- 21st October: "Weights and Measures", by Mr. N. A. Esserman.

A visit to the National Standards and Radiophysics Laboratories on 30th July was arranged through the courtesy of the C.S.I.R. The opportunity to see the work in progress in these laboratories was appreciated by members.

The Annual Dinner of the Society was held at the Sydney University Union on 31st March, 1949. There were present 98 members and friends.

The Section of Geology, whose chairman was Mr. C. St. J. Mulholland and honorary secretary Mr. R. O. Chalmers, held six meetings during the year, at which the average attendance was fourteen members and six visitors. The activities were:

- 16th April: Address by Mr. F. N. Hanlon.
- 21st May: Notes and Exhibits by Miss F. Quodling and Messrs. N. C. Stevens, C. St. J. Mulholland, H. O. Fletcher and R. O. Chalmers.
- 23rd July: Exhibit by Mrs. K. Sherrard and an address by Dr. L. E. Koch.
- 27th August: Address by Dr. J. A. Dulhunty.
- 17th September: Address by Dr. G. D. Osborne and Mr. P. B. Andrews.
- 19th November: Address by Dr. L. E. Koch.

The Council of the Society held ten ordinary meetings and one special meeting during the year, at which the average attendance was 13. The special meeting of the Council was held to discuss the "Freedom of Science". It was resolved that at the time no action beyond remaining vigilant appeared desirable, but a motion defining the Council's attitude was recorded in the minute book.

The Council has decided that in future the Annual Report, Financial Statement and List of Members will be published in Part I of the Journal, and that the abstract of proceedings of meetings will be omitted. This will effect more prompt publication of the reports and eliminate some duplication.

Professor O. U. Vonwiller and the Rev. D. J. K. O'Connell were given leave for periods of travel abroad. Among other activities, they represented Australian Science at the Zurich meeting of the International Astronomical Union. Professor Vonwiller represented the Society at the celebration in Sweden of the one hundredth anniversary of the death of Jacob Berzelius. Mr. W. B. Smith-White was elected to the office of Honorary Editorial Secretary rendered vacant by the resignation of Professor Vonwiller.



The President, Dr. R. L. Aston, has represented the Royal Societies of Australia on the National Co-operating Body in Natural Sciences of UNESCO. At the A.N.Z.A.A.S. Conference, January, 1949, at Hobart, the Society was represented by Drs. R. L. Aston, A. Bolliger and C. J. Magee. At the Seventh Pacific Science Congress, which was held in New Zealand, February, 1949, the Society was represented by Dr. Dorothy Carroll.

Dr. A. B. Walkom was one of Australia's representatives at the General Assembly of UNESCO at Beirut, and was president of the Hobart meeting of the Australian and New Zealand Association for the Advancement of Science in January, 1949.

Professor K. E. Bullen has been elected as a Fellow of the Royal Society.

On Science House Management Committee the Society was represented by Messrs. H. O. Fletcher and F. R. Morrison, with substitute representatives Dr. R. L. Aston and Mr. H. H. Thorne.

Science House Extension Committee has been working on the proposals for the eventual extension of Science House to York Street North, the representatives of the Royal Society of New South Wales being Drs. A. Bolliger and R. L. Aston.

The Clarke Memorial Lecture for 1948 was delivered by Sir Douglas Mawson, O.B.E., D.Sc., F.R.S., on 15th July, the title being "The Sedimentary Succession of the Bibliando Dome: Record of a Prolonged Proterozoic Ice Age".

The Liversidge Research Lecture for 1948 was delivered by Professor Ian Lauder, M.Sc., Ph.D., on 19th August, on "Some Recent Work on the Separation and Use of Stable Isotopes".

The Clarke Memorial Medal for 1948 was awarded to Dr. Arthur B. Walkom, Director, Australian Museum, Sydney, in recognition of his contributions to natural science, and particularly for researches in paleobotany.

The Clarke Memorial Medal for 1949 was awarded to the Rev. H. Montague Rupp for his work on Australian orchids.

The Royal Society's Medal was awarded to Professor W. L. Waterhouse, M.C., D.Sc.Agr., D.I.C., F.L.S., in recognition of his valuable researches in the field of agriculture.

The James Cook Medal was awarded to Professor Bernado A. Houssay, of the Instituto d Biologia y Medicina Experimental, Buenos Aires, Argentina, for his distinguished work for science and human welfare in the southern hemisphere, particularly through his contributions to endocrine research.

The Edgeworth David Medal, which is for Australian research workers under thirty-five years of age, was awarded for the first time. It was decided to make a joint award to Mr. R. G. Giovanelli, M.Sc., for his work in astrophysics, and Mr. E. Ritchie, M.Sc., for his work in organic chemistry.

The initiation of the James Cook Medal, in 1948, and the Edgeworth David Medal completes the scheme of the Society's awards which has been envisaged in recent years.

During the year several scientists from overseas visited the Society's rooms and were entertained by the President. Among these were:

Sir Harold Hartley, now Chairman of the British Overseas Airways Corporation (23rd November, 1948).

Sir Henry Tizard, who visited Australia at the invitation of the Commonwealth Government to advise on defence research (8th December, 1948).

Dr. Wang Ghing-Hsi, senior member of the Natural Sciences Department, UNESCO Secretariat, Paris (28th February, 1949).

Drs. A. Sison, P. Valenzuela and J. M. Feliciano, who were members of a party of Philipino scientists returning from the Seventh Pacific Science Congress in New Zealand (14th February, 1949).

Dr. S. Krishna, Lt.-Col. M. L. Ahuja, Dr. B. P. Pal and Mr. V. P. Sondhi, who were members of an Indian scientific delegation visiting Australia at the invitation of the Commonwealth Government (28th March, 1949).

The financial position of the Society, as disclosed by the annual audit, reveals the difficulties which in these years beset institutions whose income tends to remain steady but whose expenditure continues to increase obstinately despite efforts at economy which, if the tendency continues, may eventually affect the efficiency of the Society's work. The most serious example of rising costs for us is in the cost of printing the Journal and Proceedings, which in 1947 was increased from £13 to £16 per forme of 16 pages; we are now faced with an increase to £32.

The Royal Society's share of the profits of Science House for the year was £390 18s. 6d.

The grant from the Government of New South Wales of £400 has been received. The continued interest of the Government in the work of our Society is much appreciated.

The Library. The amount of £58 6s. 3d. has been spent on the purchase of periodicals, and £121 11s. 3d. on binding, the increased expenditure on binding being due to shortage of book-binding materials in 1947-1948.

Exchange of publications is maintained with 406 societies and institutions, an increase of 19 over the previous year.

The number of accessions entered in the catalogue during the year ended 28th February, 1949, was 2,501 parts of periodicals.

The Society sold its set of the *Journal of the Royal Asiatic Society of Great Britain and Ireland* to the Library, the Parliament of the Commonwealth, for the sum of £222 12s. 6d. Also, incomplets sets of medical journals were sold to Stechert-Hafner, Inc., of New York, and realized the sum of £202 5s. 11d.

Among the institutions which made use of our library through the inter-library borrowing scheme were : The University of Sydney, Department of Health, University of Queensland, Commonwealth Observatory, C.S.I.R. Food Preservation, Linnean Society of N.S.W., Forestry Commission, C.S.I.R. Plant Industry, National Standards Laboratories, M.W.S. and D. Board, McMaster Laboratory, Taubman's Paints, Elliotts and Australian Drug Co. Ltd., A.W.A. Ltd., C.S.I.R. Industrial Chemistry, Department of Agriculture, Defence Research Laboratories, Water Conservation and Irrigation Commission, Australian Paper Mills, Sydney Technical College, the University of Melbourne, Colonial Sugar Refining Co. Ltd., C.S.I.R. Aeronautics, Standards Association of Australia, C.S.I.R. Coal Survey, Sydney Grammar School, the Australian Museum, Institute of Engineers, James Hardie & Co.

R. L. ASTON,  
President.

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**THE ROYAL SOCIETY OF NEW SOUTH WALES.**  
**BALANCE SHEET AS AT 28th FEBRUARY, 1949.**

**LIABILITIES.**

1948.						1949.					
£						£	s.	d.	£	s.	d.
189	Accrued Expenses	..	..	..	..				141	5	9
25	Subscriptions Paid in Advance	..	..	..	..				26	5	0
	Life Members' Subscriptions—Amount carried forward	..	..	..	..				90	0	0
102	James Cook and Edgeworth David Medals—										
200	Amount carried forward	..	..	..	..				—		
	Trust and Monograph Capital Funds (detailed below)—										
	Clarke Memorial	..	..	..	..	1,960	4	7			
	Walter Burfitt Prize	..	..	..	..	1,055	17	5			
	Liversidge Bequest	..	..	..	..	707	10	3			
7,173	Monograph Capital Fund	..	..	..	..	3,520	18	4			
									7,244	10	7
25,877	ACCUMULATED FUNDS	..	..	..	..				26,081	18	2
(902)	Contingent Liability—In connection with tenancies of the Australian National Research Council and the Pharmaceutical Society of N.S.W.—Maximum Liability £901 16s. 8d.										
£33,566									£33,583	19	6

**ASSETS.**

1948.								1949.					
£								£	s.	d.	£	s.	d.
596	Cash at Bank and in Hand	..	..	..	..						439	14	3
	Investments—Commonwealth Bonds and Inscribed Stock, etc.—at Face Value—												
	Held for—												
	Clarke Memorial Fund	..	..	..	..	1,800	0	0					
	Walter Burfitt Prize Fund	..	..	..	..	1,000	0	0					
	Liversidge Bequest	..	..	..	..	700	0	0					
	Monograph Capital Fund	..	..	..	..	3,000	0	0					
	General Purposes	..	..	..	..	4,660	0	0					
10,860											11,160	0	0
161	Prepayment	..	..	..	..						24	2	9
	Debtors for Subscriptions	..	..	..	..	85	5	0					
	Deduct Reserve for Bad Debts	..	..	..	..	85	5	0					
14,715	Science House—One-third Capital Cost	..	..	..	..						14,745	18	6
6,800	Library—At Valuation	..	..	..	..						6,800	0	0
396	Furniture—At Cost—less Depreciation	..	..	..	..						379	0	0
29	Pictures—At Cost—less Depreciation	..	..	..	..						27	4	0
9	Lantern—At Cost—less Depreciation	..	..	..	..						8	0	0
£33,566											£33,583	19	6

## TRUST AND MONOGRAPH CAPITAL FUNDS.

	Clarke Memorial.			Walter Burfitt Prize.			Liversidge Bequest.			Monograph Capital Fund.		
	£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.
Capital at 29th February, 1948 ..	1,800	0	0	1,000	0	0	700	0	0	3,000	0	0
Revenue—												
Balance at 29th February, 1948	128	3	8	97	7	10	25	15	0	421	13	4
Interest for twelve months ..	64	13	11	34	15	0	25	15	0	99	5	0
	192	17	7	132	2	10	51	10	0	520	18	4
Deduct Expenditure ..	32	13	0	76	5	5	43	19	9	—		
Balance at 28th February, 1949 ..	£160	4	7	£55	17	5	£7	10	3	£520	18	4

## ACCUMULATED FUNDS.

	£	s.	d.
Balance at 29th February, 1948 .. .. .	25,877	0	11
Add—			
Surplus for twelve months (as shown by Income and Ex- penditure Account) .. .. .	£227	10	6
Decrease in Reserve for Bad Debts	32	7	0
	259	17	6
	26,136	18	5
Less—			
Amount written off <i>re</i> James Cook and Edgeworth David Medals	4	12	0
Bad Debts written off .. .. .	50	8	3
	55	0	3
	£26,081	18	2

The above Balance Sheet has been prepared from the Books of Account, Accounts and Vouchers of The Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 28th February, 1949, as disclosed thereby. We have satisfied ourselves that the Society's Commonwealth Bonds and Inscribed Stock are properly held and registered.

HORLEY & HORLEY,  
Chartered Accountants (Aust.).

Prudential Building,  
39 Martin Place,  
Sydney, 24th March, 1949.

## INCOME AND EXPENDITURE ACCOUNT.

1st March, 1948, to 28th February, 1949.

1947-8.		1948-9.	
£		£ s. d.	£ s. d.
507	To Printing and Binding Journal—Vol. 81 .. ..	639 13 4	
362	„ Salaries .. ..	467 15 1	
150	„ Library—Purchases and Binding .. ..	133 6 3	
90	„ Printing—General .. ..	103 9 2	
127	„ Miscellaneous .. ..	96 11 5	
95	„ Postage and Telegrams .. ..	74 0 10	
46	„ Rent—Science House Management Committee ..	54 18 5	
37	„ Cleaning .. ..	37 0 0	
23	„ Depreciation .. ..	22 16 7	
19	„ Telephone .. ..	22 3 7	
15	„ Insurance .. ..	23 11 0	
19	„ Audit .. ..	18 18 0	
12	„ Electricity .. ..	8 18 2	
18	„ Repairs .. ..	1 19 6	
	„ Reprints—		
	Expenditure .. .. £153 18 2		
	Less Received .. .. 97 9 0		
116		56 9 2	
	„ Annual Dinner—		
	Expenditure .. .. £88 13 6		
	Less Received .. .. 49 16 0		
21		38 17 6	
31	„ Conversazione .. ..	—	
1,688			1,800 8 0
—	„ Surplus for Twelve Months .. ..		227 10 6
£1,688			£2,027 18 6
1947-8.		1948-9.	
£		£ s. d.	
557	By Membership Subscriptions .. ..	586 8 6	
400	„ Government Subsidy .. ..	400 0 0	
482	„ Science House—Share of Surplus .. ..	390 18 6	
157	„ Interest on General Investments .. ..	155 12 1	
—	„ Proceeds Sale of Old Library Books .. ..	477 18 7	
—	„ Other Receipts .. ..	5 0 10	
10	„ Proportion of Life Members' Subscriptions ..	12 0 0	
82	„ Deficit for Twelve Months .. ..	—	
£1,688			£2,027 18 6

## Obituary.

ERNEST CLAYTON ANDREWS died July 1st, 1948. He was born in 1870 and had occupied a distinguished position in Australian Science for many years. He became a member of the Royal Society of New South Wales in 1909 and was a member of its Council from 1917 to 1932 except in 1919 and in 1927, during the latter of which he was invited to the United States of America to deliver the Silliman Lectures at Yale University. He was president of the Society in 1921 and was awarded the Clarke Memorial Medal in 1928 and the Clarke Memorial Lectureship in 1942.

Andrews was a graduate of the School of Geology of Sydney University, under Professor David, and joined the Geological Survey of New South Wales in 1899, becoming Government Geologist in 1920. His many published papers, twelve of them in the *Journal and Proceedings* of the Society, show a grasp of a wide variety of geological subjects, but reveal his special insight into the principles governing the evolution of physiographic features and their relation to geological structure. His work in this field in New South Wales may be said to have laid the foundation for all later researches of similar character. In the sphere of economic geology he was equally a master, and his rare geological acumen is displayed in the monumental work on the Broken Hill lode. His studies of the distribution and evolution of floras in Australia and the Pacific Islands form a contribution of high and lasting merit.

Besides his work for our Society, Andrews interested himself widely in the administration of Australian Science. Among the organisations in which he was prominent were the Linnean Society of New South Wales, of which he was president in 1937; the Australian and New Zealand Association for the Advancement of Science, Honorary General Secretary 1922 to 1926 and President in 1930; the Australian National Research Council; and the Australian Institution of Mining and Metallurgy, President 1929. On a number of occasions he represented Australian Science at important international congresses.

Andrews received many honours besides those already mentioned, among which were honorary membership of the Washington Academy of Sciences and the Geological Society of America; honorary fellowship of the Royal Society of New Zealand; the Mueller Medal of the Australian and New Zealand Association for the Advancement of Science (1946); the Lyell Medal of the Geological Society of London (1931); and the David Syme Prize and Medal of the University of Melbourne. Through it all he remained a deeply serious and generous worker among his fellow scientists, among whom he was as much esteemed for his personal qualities as he was respected for his scientific attainments.

GEORGE FREDERICK BIRKS died May 4th, 1948. He was 82 years of age and had been a member of the Society since 1923. He was a member of the party which went to Paraguay under the leadership of William Lane to found a socialist colony. After he returned to Australia he entered upon a business career, later becoming a director of several undertakings and chairman of directors of Potter and Birks, Pty., Ltd., a firm of manufacturing chemists which was founded by him. He was much interested in the Rotary movement and was a World Vice-President of the Rotary International. He was also a devoted worker for crippled children, and the Activity School at the Royal Alexandra Hospital for Children is named after him.

ERNEST NORMAN MCKIE died May 19th, 1948. He was born at Guyra, New South Wales, in 1882, and spent most of his life around the New England district.

He at first intended to take up a business career and worked with the Commercial Banking Company of Sydney. Later he resigned to enter St. Andrew's College, Sydney University, from which he graduated as Bachelor of Arts in 1906. He completed the theological course in 1908 and took his first church appointment at Manilla, whence he moved to Bendemeer in 1909 and Guyra in 1912. He served as Moderator of the General Assembly of the Presbyterian Church in 1938.

Mr. McKie was an amateur botanist of distinction and had a detailed knowledge of the eucalypts and native grasses of the New England district. His knowledge and help were always available to research workers visiting the district. Beside his interest in botany he took an active part in movements to improve the standard of agriculture in his district, being the first secretary of the local branch of the New South Wales Agricultural Bureau, and for many years associated himself with the fostering of modern trends in agricultural work.

He was a member of the Australian Institute of Agricultural Science, the Linnean Society of New South Wales, to the *Journal* of which he contributed, and since 1932 of the Royal Society of New South Wales.

EDWARD MONTAGUE WELLISH, M.A., Emeritus Professor of Mathematics of University of Sydney, died after a short illness at his home in Roseville in July, 1948.

He entered the University in 1900 from Fort Street School after a brilliant pass at the Senior Examination in December, 1899, being equal with another student for the John West and Grahame Medals for general proficiency. He attended the evening classes, his guide in mathematics being the late Assistant Professor A. Newham. He graduated with first-class honours and the University Medal in Mathematics. He and Professor C. E. Weatherburn were awarded the University Medal for Mathematics for the M.A. degree in the year 1906.

In 1907 he was awarded the first Graduate Barker Scholarship and entered Emmanuel College, Cambridge, in October of that year. He commenced research in the Cavendish Laboratory under Sir J. J. Thomson. His research was on the theory of ionisation of gases, his chief papers during this period being "The Laws of Mobility and Diffusion of Ions formed in Gaseous Media", *Proceedings of the Cambridge Philosophical Society*, November, 1908; and "The Mobilities of the Ions Produced by Röntgen Rays in Gases and Vapours", *Transactions of the Royal Society of London*, January, 1909; and "The Passage of Electricity through Gaseous Mixtures", *Proceedings of the Royal Society of London*, June, 1909.

Emmanuel College awarded him a special scholarship and a little later the excellency of his work was emphasised by the award of the Clerk Maxwell Studentship. After graduating B.A. (Research) at Cambridge, Professor Wellish accepted the post of Assistant Professor at Yale University, U.S.A. In 1913 he published in the *Philosophical Magazine* "Experiments on Columnar Ionisation" and in the *American Journal of Science* he published two papers, "The Mobilities of Ions in Air" and "The Motion of Ions and Electrons through Gases".

He returned to Sydney in 1916 and was appointed to a lectureship in the Department of Mathematics and in 1926 he was given the status of Associate Professor of Applied Mathematics. His time for research in Physics was naturally restricted, his next papers appearing in 1924 and 1931, when he published "Photo-electrons and Negative Ions" in the *Proceedings of the Royal Society of London*.

During the nine years when Professors Carslaw and Room were absent from the Department of Mathematics, Professor Wellish was in charge. He retired in 1946, but to the regret of all his friends his health improved only slightly.

Professor Wellish was outstanding in his research, his lecture work and his administrative work. He rendered signal service on the Board of Secondary School Studies. As chief examiner in Mathematics for the Leaving Certificate Examination, he was always sympathetic to school teachers and their problems. His colleagues will always remember his consideration and kindness.

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# A CONTRIBUTION TO THE STRATIGRAPHY AND PHYSIOGRAPHY OF THE GLOUCESTER DISTRICT, N.S.W.

By P. B. ANDREWS, B.Sc.,  
*Teaching Fellow in Geology, University of Sydney.*

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With one text-figure.

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*Manuscript received, January 7, 1949. Read April 6, 1949.*

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## I. INTRODUCTION.

In a recent paper (Osborne and Andrews, 1948) the geological structure of the northern end of the Stroud-Gloucester Trough was discussed. A full account of previous investigations and a geological map of the area were included in that work. The present paper deals with some aspects of the stratigraphy and physiography of the same area. The major contributions to these subjects have been those of Sussmilch (1921) and Voisey (1940), who have discussed the stratigraphy of part of the area in considerable detail. Carey and Browne (1938) and Voisey (1945) have also discussed the Carboniferous succession at Gloucester and have correlated it with those of other areas. The following notes are intended primarily to extend the work of these investigators, particularly to the areas immediately to the south and east which have an important bearing on the final elucidation of the geology of this interesting district.

## II. STRATIGRAPHY.

### (a) *Carboniferous.*

Sussmilch (1921) described a section across the Carboniferous strata on the west side of the Gloucester Trough in the neighbourhood of Barrington village and divided the sequence into the marine Burindi Series and the overlying terrestrial Kuttung Series. Carey and Browne (1938) further subdivided the Burindi Series into lower and upper sections, the Upper Burindi Series being the marine equivalent of the terrestrial Lower Kuttung Series of the Hunter River type area. Voisey (1940) described further sections from the same locality.

The recognition of a large fault separating the Devonian and Lower Burindi strata on the western side of the Trough (Osborne and Andrews, 1948) has confirmed the fact that the base of the Burindi Series is not exposed in these sections. The conglomerates outcropping on the Giro and Copeland Roads which are mentioned by Sussmilch and Voisey appear, however, to be close to the base of the series. A greater development of these conglomerates occurs

on the western side of the Barrington River on the "Manchester" Road, and here the following section was measured in descending order :

	Feet
Conglomerate and tuff .. .. .	220
Tuff .. .. .	165
Mudstones .. .. .	10
Tuff and tuffaceous conglomerate .. .. .	35
Tuffaceous conglomerate and mudstones .. .. .	120
Tuff .. .. .	15
Coarse conglomerate .. .. .	60
Tuff .. .. .	30
Tuffaceous conglomerate .. .. .	70
Tuffs and mudstones .. .. .	85
Tuff .. .. .	50
Conglomerate .. .. .	15
Tuffs and mudstones .. .. .	85
Conglomerate .. .. .	25
Tuffs and mudstones .. .. .	80
Total .. .. .	<hr/> 1,065 <hr/>

The lowest beds in this sequence are separated by the Manchester Fault from Devonian rocks which outcrop on the flank of Mechanic's Mountain a short distance to the east. Figure 1 shows a columnar section of the Carboniferous strata in this neighbourhood and includes a revised estimate of the upper part of the Carboniferous sequence for the western side of the Stroud-Gloucester Trough.

The series which is shown in Figure 1, and which represents essentially the sections measured by previous workers, can be traced from the Bowman Road Fault, about  $2\frac{1}{2}$  miles west of Gloucester, westwards to Barrington village, and thence southward to the Rawdon Vale Road in the vicinity of Cut Hill, where the beds appear to be cut off by an East-West fault.

Work in the area between the Rawdon Vale Road and Spring Creek on the western side of the Trough, and also on the eastern side between the Gloucester-Taree road and Ward's River, has shown, however, that this type section is not developed in any other part of the Gloucester-Stratford district, and none of the datum beds which have been referred to have been located elsewhere in the area.

Owing to the extensive faulting which has taken place, it was found impossible to measure a complete section of the Carboniferous Series on the eastern side of the Trough. Strata of Lower Burindi age outcrop in the country immediately to the south of the Gloucester-Krambach road from a point near the junction of the Mograni Creek road, east at least as far as Gangat, being cut off by faults from Devonian strata to the north and Upper Kuttung and Upper Burindi rocks to the south. These beds consist of mudstones and tuffs dipping steeply to the north. In Brushy Cutting near Gangat a thick series of greenish-grey friable mudstones with subordinate thin bands of tuff is exposed along the road. These beds closely resemble those of the Lower Burindi Series on the west side of the Trough. No fossils have been found in them.

An approximate section of the Upper Burindi and Upper Kuttung rocks on the eastern side of the Trough was measured from Mograni Creek School in a westerly direction. This revealed a total thickness of about 7,400 feet for the Upper Burindi Series, consisting essentially of felspathic and pebbly tuffs and mudstones. These beds are very similar to those of the Upper Burindi Series

on the western side of the Trough, but no fossils were found in them. Over much of this area the beds are dipping vertically, and it is probable that some strike faulting has occurred, thus accounting for the very great thickness measured for the series.

About halfway up in this section is a flow, about 20 feet thick, of green dacitic pitchstone which was traced along its strike for about  $1\frac{1}{4}$  miles but lenses out. Under the microscope the groundmass of this rock is seen to be partly glassy, but is crowded with microlites. A few corroded phenocrysts of quartz are scattered through the rock, and clusters of oligoclase phenocrysts are also present. This may possibly be correlated with a very similar flow which outcrops for a short distance on the ridge to the south of the Rawdon Vale road, where it crosses Cut Hill, where it immediately underlies the topmost flow of quartz-keratophyre in the Upper Burindi sequence.

The top of the first main ridge in the Mograni section is composed of a coarse tuffaceous conglomerate which was considered to be the basal bed of the Upper Kuttung Series, the overlying beds consisting almost entirely of pebbly tuffs and conglomerates in which some obscure plant remains were found. Farther to the south Upper Burindi strata outcrop along the Waukivory Road, and here consist of mudstones and light-coloured coarse felspathic tuffs. Marine fossils were found in Portion 211, A. A. Coy's Grant, close to the road, in a locality mentioned by Voisey (1940). These were not sufficiently well preserved for identification, but included pelecypods and a small gastropod. On the ridge between this point and Phillip's Creek a bed of coarse tuff was found which contains crinoid stems, but most of the considerable thickness of pebbly tuffs and mudstones are apparently unfossiliferous. The presence of the East Stratford Fault, which separates these beds from the Upper Kuttung Series, prevents the determination of the exact position in the sequence of the fossiliferous horizons.

The rugged country at the head of Dog Trap Creek and Ward's River consists of a great thickness of apparently unfossiliferous tuffs and tuffaceous conglomerates with subordinate mudstones. The ridge on which is situated Craven Trigonometrical Station is formed of one of the beds of coarse tuffaceous conglomerate. These sedi-

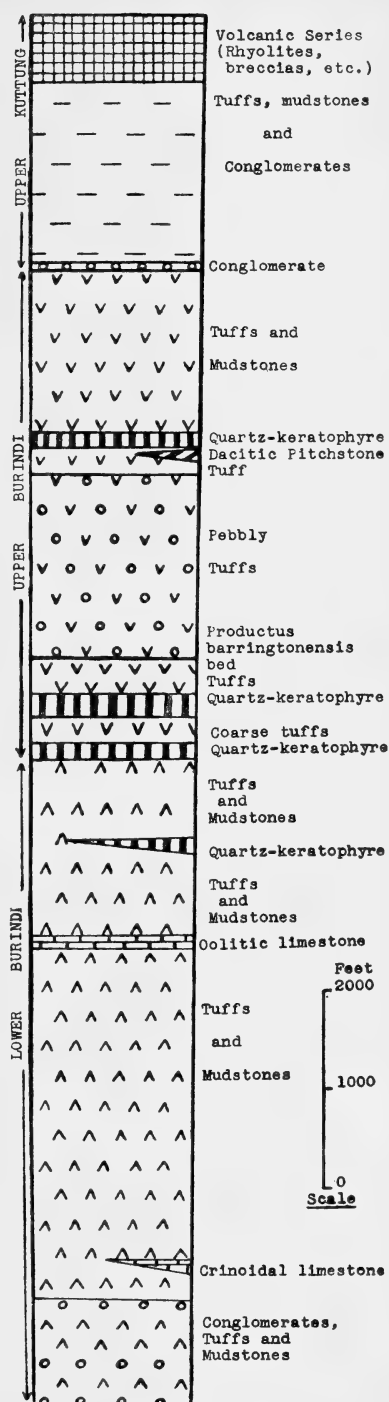


Fig.1. Generalised Section of Carboniferous Strata on western side of Stroud-Gloucester Trough.

ments are again very similar to those of the Upper Burindi Series on the western side and are provisionally correlated with them. In this neighbourhood the strata dip to the east at angles of about 70 degrees and are cut off on the west by the East Stratford Fault.

The steep ridges on the western side of the Stroud-Gloucester Trough, south of the Rawdon Vale road, also consist almost entirely of pebbly tuffs. However, a flow of rhyolite forms the highest part of the ridge between Cut Hill Creek and the upper Avon River. South of the Avon River the crest of the Faulkland Range is formed of another thin flow of acid lava, in this case a light grey, wholly glassy rock with numerous veinlets of quartz. Here, however, the associated sediments, which include dark-coloured cherts and a few thin beds of carbonaceous shale, appear to belong to the Upper Kuttung Series. Pebbly tuffs and mudstones which outcrop on the western flank of the Faulklands Range are believed to be of Upper Burindi age, but no detailed work was carried out in this locality.

Carey and Browne (1938) suggested that the type section of the Upper Burindi Series on the western side of the Gloucester Buckets Range was a predominantly terrestrial sequence with thin marine intercalations. Voisey (1945) considers that the whole of the Upper Burindi Series is marine. A careful study of these beds has shown that fragments of marine fossils are widely distributed through the series, but it is possible that there are some terrestrial sediments interbedded in an essentially marine sequence. It must be emphasized that the whole facies is indicative of shore-line conditions.

The almost complete absence of marine fossils from the corresponding beds on the eastern side of the Trough may indicate that this particular area was one of predominantly terrestrial deposition, the same types of tuffs and pebbly beds being present as in the marine series on the western side. It is also significant that no marine fossils have been found in similar beds on the western side farther south than the Rawdon Vale road.

Thus it is probable that much of the strata indicated on the previously published map (Osborne and Andrews, 1948) as belonging to the Upper Burindi Series is, in fact, of terrestrial origin. As the distinction is purely one of facies and not of age it has been considered advantageous to classify all these rocks under a single head.

The most notable feature of the Upper Kuttung Series in the Gloucester-Stratford district is the great development of volcanic rocks. These have been discussed by Sussmilch (1921) under the name of the "Gloucester Rhyolites", but Voisey (1945) has pointed out that the greater part of the volcanic series consists of fragmental material. This is particularly the case on the eastern side of the Stroud-Gloucester Trough where these strata attain their greatest development. The total thickness of the volcanic series in the neighbourhood of Mograni Mountain is about 3,000 feet. No attempt has been made to map individual flows, of which there are a large number, but many different varieties have been collected. A great deal of brecciated material is present, the fragments consisting largely of banded rhyolites and tuffs of several kinds. Many of the lavas exhibit large vughs and veins filled with chalcedony, and it is interesting to note that this is also the case at Pokolbin, where lavas occur which are almost identical chemically with some of those of the Gloucester Buckets Range. The lavas range in composition from rhyolites to andesites, blue dacites showing strong flow structure being particularly well developed in the vicinity of Oak Creek Falls.

The Upper Kuttung Series to the west of Stratford and Craven consists almost entirely of tuffs and tuffaceous conglomerates, and the typical volcanic sequence is not developed, although it still appears in the ranges on the east

side of the valley. At the head of the Upper Avon road, pink and purplish volcanic breccias outcrop, but these are of an entirely different type from the brecciated lavas of Mograni Mountain.

(b) *Permian.*

Rocks of Permian age occupy the central part of the Stroud-Gloucester Trough and consist of conglomerates, grits, sandstones, shales and coal seams. These beds have been assumed to belong to the Upper Coal Measures (Sussmilch, 1921 ; Voisey, 1940) but no direct correlation can be made as they are isolated from the main coal basin of the Hunter River Valley and a correlation based purely on lithological similarities cannot therefore be accepted.

Owing to the presence of much minor folding and variations in dip, and to the paucity of good outcrops, the thickness of the Coal Measures cannot be accurately measured, but in the neighbourhood of Gloucester there is a total thickness of at least 1,900 feet. No clearly defined junction between these beds and the underlying Upper Kuttung Series has yet been found, owing to the characteristic talus slopes which everywhere mark the boundary of the volcanic series, but in a track cutting close to the Barrington River near Kiaora Crossing, and in the railway cutting immediately north of the bridge over the Avon River, the two series appear to be separated by an erosional disconformity, the Permian rocks occupying hollows in the surface of the Upper Kuttung lavas. The basal bed of the Permian sequence wherever studied is a coarse conglomerate containing pebbles of rhyolite and tuff which gives further evidence of a probable erosional break between the two series.

The best exposures of the Coal Measures are to be seen in the railway cuttings between Spring Creek and Craven, in the southern part of the area under discussion. A large number of outcrops of coal seams appear in these cuttings, but most of the seams are very thin. These beds show many minor folds and faults (Osborne and Andrews, 1948). In the bed of Coal Creek about one-quarter mile south of Craven Railway Station a section was measured totalling 146 feet of sediments, of which 24 feet is coal, but this is distributed between thirteen distinct seams.

To the east of Craven, along the Glen road and south at least as far as Stoney Creek, is a faulted outlier of Coal Measures consisting essentially of sandstone and conglomerate. A 14-foot seam of coal is exposed in the bed of Stoney Creek a short distance above its confluence with Ward's River.

### III. PHYSIOGRAPHY.

Sussmilch (1921) briefly discussed the major physiographic features of the Gloucester district and mentioned the contrast between the relatively flat and low-lying valley of the Gloucester, Avon and Ward's Rivers, excavated in soft Permian strata, and the steep country on either side occupied by Carboniferous rocks.

Extensive alluviation of the lower reaches of the Gloucester and Avon Rivers at the northern end of the valley has taken place, and this is probably partly due to the blocking of the Gloucester River immediately above its junction with the Barrington River by a hard bar of Carboniferous lavas which is an extension of the Mograni Range. This would have formed a local base-level for the river. This is confirmed by the presence of a river terrace which is revealed in a road cutting where the river passes on the north side of the town of Gloucester and which is about 40 feet above the present river level.

In the main valley, the divide between the Avon River system flowing northward and the Ward's River system flowing to the south is very low and

irregular. Ward's River flows out of the ranges on the eastern side in a narrow valley at an average elevation about 100 feet lower than the land immediately to the north, and its tributaries, cutting back in this direction, threaten to capture the headwaters of Swamp Creek which now flows over an almost level plain before joining the Avon River. In a similar way Spring Creek, which flows into Ward's River from the west, threatens to capture the heads of some of the small creeks which flow northward to the Avon River on the western side of the North Coast Railway. If these changes were to take place the whole drainage pattern of the Avon River would be reversed.

Sussmilch noted that the main stream channels appear to antedate the present topography, and it may be noted that this also applies to many of the smaller streams, which have cut across hard and weak structures alike. On the eastern side of the main valley Ward's River, Waukivory Creek, Dog Trap Creek and Mograni Creek all rise in the country to the east of the Mograni Range and have cut steep gorges through it as they flow westward, cutting at right angles across the general trend of the country to do so. Waukivory Creek flows in a relatively mature valley on the eastern side before plunging into a narrow gorge through the range, which rises to a height of over 1,000 feet on either side.

In the same way the Gloucester River and Gap Creek have cut through the Gloucester Buckets Range on the western side. The case of Gap Creek is particularly noteworthy, as it rises in low hills within a mile of the Barrington River, but flows eastward by way of a deep and narrow gorge through the Gloucester Buckets into the Gloucester River.

The course of the Barrington River is of great interest. Between Berrioc and Faulklands are a series of entrenched meanders, but at the latter locality the river turns sharply and flows northward, approximately parallel to the strike of the Carboniferous strata. Where the strike of these rocks swings round to the east in the vicinity of Barrington village the river continues northward for another mile and then turns sharply to the east. Farther downstream the river flows approximately parallel to the strike of the Devonian strata on the northern bank, but here its course is determined primarily by the presence of the Barrington River Fault. The reasons for the two abrupt changes of course are difficult to visualize, but that at Faulklands may have been caused by piracy of the head of the old river by a young stream cutting back along the strike from the north, the old river having previously flowed to the east, as is still the case with the Gloucester River.

#### IV. CONCLUSION.

The above notes are intended primarily to extend the work of previous investigators and to present some aspects of the stratigraphy and physiography of the Gloucester-Stratford district which have not previously been discussed. It is emphasized that the important Carboniferous sequence of the western side of the Stroud-Gloucester Trough, which has been the subject of much discussion is developed only within a comparatively limited area, and in particular is not found on the eastern side of the Trough in the neighbourhood of Gloucester.

#### V. ACKNOWLEDGEMENTS.

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## THE EFFECT OF DIFFUSIONAL PROCESSES ON THE RATE OF CORROSION.

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### LIMITATIONS OF CORROSION TESTS.

Reviews of corrosion test procedure by White (1934), McKay and La Que (1937), La Que and Knapp (1945) and by others have stressed the necessity for a very close standardization of conditions. If measurements of the rate of loss of mass from a metal test piece in a given corrodant liquid are to be any guide to the behaviour of metal members under large-scale conditions, very close attention must be paid to a number of details, such as the depth of immersion, the methods of suspension or support and the conditions of aeration and circulation of the fluid ; as well as to such more obvious factors as the temperature and pH of the corrodant liquid and the presence or absence of other metals forming electro-chemical couples with the test specimen. White, indeed, has emphasized the difficulty in getting reproducible results even with different specimens of the same dimensions, and La Que and Knapp have stressed the necessity for a detailed evaluation of the proposed conditions of application in order that these may be duplicated as closely as possible in the laboratory tests.

The overall reaction of a metal dissolving in an electrolyte to give either a soluble or insoluble ionic product has long been recognized as a complicated one. Many successive physical and chemical operations are involved. Much attention has recently been given to some of these operations, especially those of a more chemical nature, such as interphase ionic transfer, anodic and cathodic polarization, and the effect thereon of inhibitors and accelerators. On the other hand the effect of the transport processes which bring the active depolarizing agent up to the seat of attack and remove therefrom the products of reaction has not received such close attention. It is clear, for example, that in the corrosion of copper by acetic acid in which the reaction is maintained by cathodic depolarization produced by dissolved oxygen, the maintenance of the chemical attack is dependent on the continuity of the supply of oxygen to the cathodic areas ; and it is conceivable that, under certain conditions, the rate of diffusion of oxygen might become a rate determining factor.

The conception of a set of physical transport phenomena entering into the final determination of the rate of chemical attack by a corrodant liquid is one which has been paralleled in recent years in other fields of applied chemistry. Thus Damköhler (1936), Edgeworth Johnstone (1939), Laupichler (1938), Hurt (1945) and Bosworth (1947) have all discussed the effect of such factors as the flow of heat and flow of reactants and resultants on the course of chemical reactions in small and large scale reactors. Further, Agar and Hoar (1948) have discussed the effect of a change of scale on an electrochemical system and have concluded that the rate controlling step for a large scale system is not necessarily the same as for a small scale system under otherwise identical chemical and physical conditions.



## VARIABLES OF THE TRANSPORT PROCESS.

It appears desirable, therefore, to examine the process of corrosion with a view to enumerating and, if possible, devising methods of measuring the factors which are concerned in the transport of matter to and from the corroding surface. In this object there is one obvious mode of attack. Recently a number of authors (Sutton, 1934 ; Powell and Griffiths, 1939 ; Pasquill, 1943 ; and Boelter, Gordon and Griffin, 1946) have traced a degree of parallelism between heat loss and loss of matter by evaporation from geometrically similar bodies. Since it is not unreasonable to expect that matter loss from corroding bodies might also behave similarly, and further since the laws of conduction and convection of heat are particularly well known, the first object of this paper and of the two succeeding papers will be an attempt to trace a degree of parallelism between heat loss and matter loss by corrosion from geometrically similar bodies. This paper will be specifically concerned with transport under stagnant fluid conditions, analogous to the transport of heat in a fluid by thermal conductivity alone.

The corrosion rate  $q$ , in mass flow per unit area per unit time, and the corrosion cell e.m.f.  $E$  are, clearly, two of the properties with which we will be concerned. The quantity  $E$  is the driving force which produces a flow of matter  $q$ . While much has been discovered from purely electrochemical measurements concerning the mechanism whereby  $E$  produces the matter flow  $q$ , we are not here immediately concerned with this subject. We are, however, concerned with the property which might be defined as the overall chemical resistance (or impedance) of the system—that is to say the factor which determines the magnitude of the driving force required to produce a given flow rate. Since various successive reactions are involved in the corrosion process, this overall resistance can presumably be split into a number of series (or parallel) components, one corresponding to each step in the corrosion process ; in much the same way as the flow of heat in a multi-component system can be represented by a number of series (or parallel) thermal resistances. Among the factors contributing components to the overall chemical resistance are the transport processes leading to the removal of the anodic and cathodic products of corrosion from the immediate vicinity of the interface under attack. Removal may be effected by diffusion, turbulent diffusion, or by the convection currents set up either as a result of density changes produced by the solution of heavy metal ions, or from temperature changes. Since the mechanism of removal of the products of reaction controls the degree of polarization, it also controls the magnitude of the electric current across the metal-electrolyte interface and thus the rate of corrosion. The transport processes involved in the removal of matter from the vicinity of the interface bear a formal similarity to those exhibited by the heat loss from a hot body immersed in a fluid. Heat may be carried from such a body by molecular conduction, turbulent conduction, by forced convection if the fluid is stirred, or by natural convection.

Examples of corrosion in which an insoluble phase resulting from chemical reaction consequent to corrosion builds up a barrier to the diffusion process, or those in which the corrosion reaction is maintained by the presence of a bimetallic system providing a permanent cell e.m.f. obviously involve a transport mechanism which is more complicated than that involved in the flow of heat. However, when uniform, or general corrosion alone occurs, it would appear that the transport processes have features in common, and it is this suggested similarity which will be discussed below.

## EXPERIMENTAL.

The subjects of experimentation were selected so as to avoid the more complicated types of corrosive attack. The subjects consisted of copper,

certain copper alloys and steels in acetic acid-acetic anhydride mixtures. Commercial acetic acid has a high electrical resistivity of the order  $1.5 \times 10^{-6}$  ohm-cms., and accordingly bimetallic corrosion is not serious. The acetates are soluble, and thus complications due to the formation of barriers are avoided. Further, experience has shown that these systems do not show the phenomenon of dezincification in which one component of an alloy selectively dissolves. The only type of corrosion is a general attack all over the surface exposed to the acid. Accordingly these systems are particularly suitable for the examination of the influence of convection on the process of corrosion.

The equipment used consisted of a cylindrical body C of the metal under test, 3 cms. in diameter and 1.8 cms. long. One flat face of this body contained a cylindrical hole 1.0 cm. in diameter and 0.8 cm. deep coaxial with the body as a whole. Into this hole there fitted snugly a second cylinder, B, of the same metal, the two top faces being coplanar. These two faces were polished together. Cylinder B was removed and weighed and then placed back in position. The air was pressed out through a hole at the back of C, and this hole was finally closed by means of a screw also of the same metal. A thin film of an acid-proof grease used for lubrication prevented the corrodant from coming into contact with any portion of B other than the front face. This equipment thus permitted a study of the attack on a definite area of a single metal face surrounded on all sides by a surface of the same metal, which thus acted as a guard ring and, by eliminating irregularities in the field of the corrodant at the edges, reduced the geometrical pattern of the flow of matter to and from the face under attack to one in a single dimension.

After subjection to the corrosive conditions for a measured time, cylinder B was removed, the acid-proof grease was dissolved in a volatile solvent and the cylinder dried and weighed.

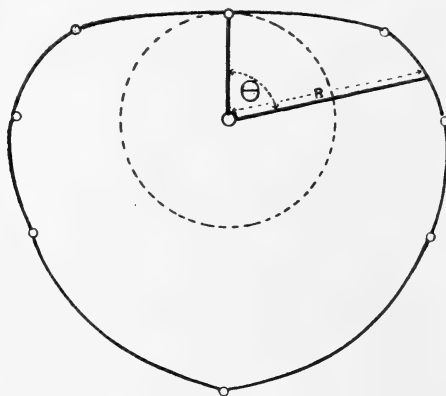


Fig. 1.

#### THE EFFECT OF ORIENTATION.

The equipment as described above was first used in a study of the effect of orientation on the rate of corrosion. An iron (mild steel) surface was immersed 4 cms. in a 60/40 acetic acid-acetic anhydride mixture and the rate of corrosion measured at different orientations as the face was turned in a vertical plane through  $2\pi$ . The results are shown in the form of a vector diagram in Figure 1. In this diagram the  $r$  co-ordinate measures the rate of corrosion and the  $\theta$  co-ordinate the azimuth.

It will be seen from the figure that the rate of loss of matter is a minimum when the corroding surface is facing upwards and a maximum when facing downwards. Evans and Mears (1934) have already remarked on the flow of heavy metal salt solution under gravity away from all surfaces except those facing vertically upwards. This flow constitutes a convection current opposite in direction, but essentially similar in nature, to the convection currents surrounding a hot body in a fluid. Thus it is seen from Figure 1 that the corrosion rate is a maximum when the convection current is most intense and a minimum when there is no convection and when the loss of matter takes place entirely by a "conductive" mechanism.

In taking measurements of the corrosion rate with all transport processes restricted to those of the "conductive" type, it is of importance to be able to estimate the error involved in any slight departure of the surface from the horizontal position—say by an angle  $\theta$ . Since the top of Figure 1 is flat, it follows that the error is of the order  $q/\cos \theta$  or  $q(1+\theta^2)$ , where  $q$  is the measured rate. Errors of magnitude sensible in comparison with the random errors usual even in the best corrosion measurements are thus not incurred unless  $\theta$  is greater than  $0.2$  radian or  $12^\circ$ , which quantity is thus a measure of the tolerance allowed on the orientation.

#### EFFECT OF VARYING THE DEPTH OF IMMERSION.

The property of thermal conductivity plays a large part in all successful attempts at the co-ordination of experimental determinations on the rate of conductive and convective transfer of heat. If a similar co-ordination of the effects of convection on the corrosive transfer of matter is to be attempted, it is

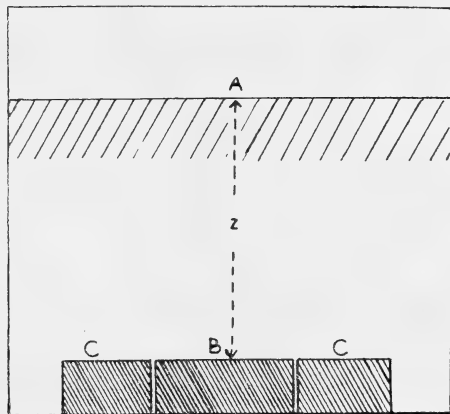


Fig. 2.

important to find that property concerned with the transport processes involved in corrosion which plays the same part as thermal conductivity does to heat flow in fluids. Such a property could be measured by an adaption of the guard-ring method of measuring thermal conductivity. If we set up the equipment, described in the section above, horizontally at a distance  $z$  below a free surface, we will effectively be concerned with one-dimensional diffusion through a distance  $z$ , the depolarizing agent (atmospheric oxygen) having to travel that distance through a stagnant layer of the corrodant liquid.

In Figure 2, let  $A$  represent the free surface of the corrodant and  $B$  and  $C$  respectively the surface under attack and the guard-ring both at a distance  $z$  from the free surface and parallel to it. We are concerned with a flow of matter

from B to the liquid; the flow, on account of the influence of the guard-ring, being normal to the surface. This flow, the magnitude  $q$  of which may be measured by weighing the central cylinder before and after a measured time interval, is stoichiometrically connected with all chemical steps in the corrosion reaction. One of these steps is the "conductive" flow of the depolarizing agent through a distance  $z$ . The magnitude of  $q$  therefore might be expected to vary with  $z$  in the same way as the flow of heat from a geometrically similar hot plate separated from another plate, at a temperature difference  $\theta$  from the former, by a convectionless thermal conductor of conductivity  $k_\theta$ . In such a thermal system the heat flow  $q_\theta$  per unit area per unit time is related to  $\theta$  by an equation:

$$k_\theta = \frac{q_\theta z}{\theta}.$$

If  $dq_\theta$  is the heat flow change associated with a change  $dz$  in the thickness of the thermal conductor, we have

$$k_\theta = \frac{1}{\theta} \frac{dz}{d(1/q_\theta)} \dots\dots\dots (1)$$

In the mass flow system involved in the corrosion process we may readily measure the change in the rate of corrosion ( $dq$ ), in units of mass crossing unit area in unit time, produced by a change  $dz$  in the length of the path through which the depolarizing agent is conducted. In this system now we may define a corresponding conductivity term  $k_c$  by means of an expression analogous to equation (1), viz.

$$k_c = \frac{1}{E} \frac{dz}{d(1/q)} \dots\dots\dots (2)$$

where by  $E$  is to be understood the overall driving force for the corrosion reaction, or the corrosion cell e.m.f.

If for a given system  $k_c$  is a constant, or if in other words the system follows a law analogous to Fourier's law, then we expect to get a straight line when the depth  $z$  is plotted against the reciprocal of the rate of corrosion ( $1/q$ ). Experimental data obtained on the guard-ring equipment are represented in Figures 3 and 4, where  $1000/q$  is plotted against  $z$  for the different systems studied. The experiments were conducted in a thermostat at two different temperatures, namely 20° C. and 70° C. The  $1/q$  versus  $z$  lines are straight, but do not pass through the origin. Each system may thus be described by two constants; the intercepts  $1/q_0$  on the  $1/q$  axes which incidentally are always positive, and

the slopes  $\left( \frac{dz}{d(1/q)} \right)$ , which we shall denote hereunder by the symbol  $j$ . We

see, therefore, that the process of transport of matter involved in a corrosion reaction taking place under "conductive" conditions involves two properties of the system,  $j$  and  $q_0$ . The significance of these properties will be discussed below, but first it is desirable to consider the units in which these quantities are to be measured and the magnitude of these properties for typical systems.

#### UNITS.

Many problems connected with the transport of matter and of heat which are too complicated for a complete mathematical treatment have been successfully treated by the use of dimensionless quantities. In order to combine the quantities connected with the transport phenomena concerned with corrosion, it is first necessary to use a consistent set of units throughout. The various phenomena involved can be reduced to four fundamental dimensions. Now  $q$  the rate of corrosion is, in the technical literature, commonly measured in units

of milligrammes decimetres<sup>-2</sup> days<sup>-1</sup>, while  $E$ , the corrosion cell e.m.f., is commonly measured in volts. We shall accordingly take for our four fundamental units the quantities, decimetres, milligrammes, days and volts. Thus the quantity  $j$  above is to be measured in milligrammes decimetres<sup>-1</sup> days<sup>-1</sup>, while  $k_c$  is to be measured in milligrammes decimetres<sup>-1</sup> days<sup>-1</sup> volts<sup>-1</sup>.

The units in which the other properties of importance are to be measured will be given later. For convenience this system of units will be referred to as the d.m.d.v. system.

### RESULTS.

The experimental results calculated from the lines shown in Figures 3 and 4 are tabulated in Table 1. For each system and temperature studied the two properties  $j$  and  $q_0$  are recorded, each of course, in d.m.d.v. units.

TABLE 1.

Metal.	Corrodant.	Temperature.	Slope $j$ Milligrammes dm <sup>-1</sup> , day <sup>-1</sup> .	Reciprocal Intercept $q_0$ Milligrammes dm <sup>-2</sup> , day <sup>-1</sup> .
Copper.	Acetic anhydride .. .. .	20° C.	9.6	51
"	60/40 acetic acid/acetic anhydride	"	10.5	125
"	Glacial acetic acid .. .. .	"	13.8	150
"	50% aqueous acetic acid .. .. .	"	6.0	97
"	50/50 acetic acid/benzene .. .. .	"	195	405
"	60/40 acetic acid/acetic anhydride	70° C.	190	2000
"	Glacial acetic acid .. .. .	"	710	2000
Brass.	Acetic anhydride .. .. .	20° C.	1.6	71
"	60/40 acetic acid/acetic anhydride	"	6.2	66
"	50% aqueous acetic acid. .. .. .	"	3.3	70
Phosphor bronze.	60/40 acetic acid/acetic anhydride	20° C.	18.2	135
"	Glacial acetic acid .. .. .	"	20.0	130
"	50% aqueous acetic acid .. .. .	"	16.0	100
"	Glacial acetic acid .. .. .	70° C.	660	1050
Mild steel.	60/40 acetic acid/acetic anhydride	20° C.	52.0	1000
"	Glacial acetic acid .. .. .	"	62.0	950

### DISCUSSION.

The lines represented on Figures 3 and 4 relating the variation of the rate of corrosion with the depth can be put in the form

$$\frac{1}{q} = \frac{1}{q_0} + \frac{z}{j} \dots\dots\dots (3)$$

A similar expression would have been given for the heat loss across a thermal conductor of various thickness from a hot body, which however is not bare but thermally lagged so that the rate of heat loss can never exceed a certain figure.

The property  $j$  is related to the correction conductivity  $k_c$  by the expression

$$j = Ek_c \dots\dots\dots (4)$$

and is more convenient than  $k_c$  because the quantity  $E$  is not directly concerned in corrosion measurements. The quantity  $j$  is a measure of the conductivity of the corrodant for the depolarizing agent and is thus a measure of a sensitivity of

the reaction concerned to control through limiting the supply of depolarizing agent. A reaction giving a small  $j$  such as brass in acetic anhydride is strongly dependant on the supply of atmospheric oxygen.

The quantity  $q_0$  is a measure of the rate of corrosion when the depolarizing agent is made instantly available at the surface and is thus a quantity of more direct chemical significance than measures of  $q$  under any standard conditions of

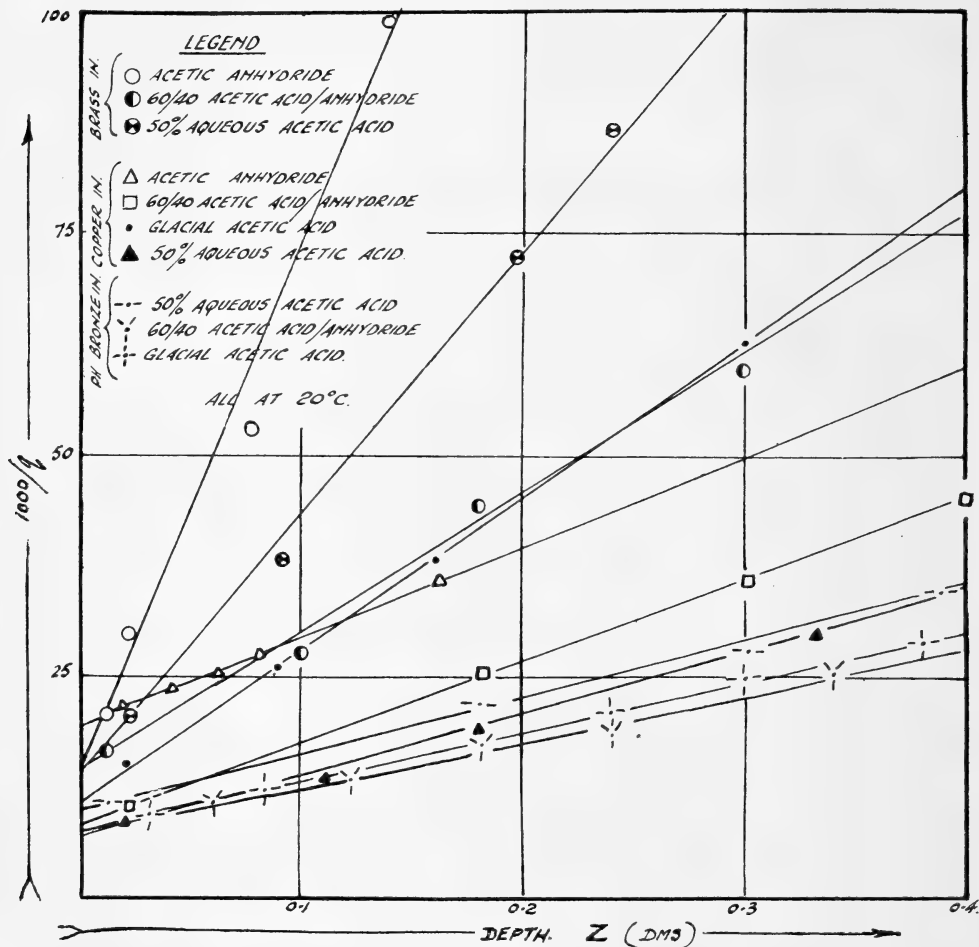


Fig. 3.

immersion or aeration. The ratio  $E/q_0$  is a measure of the resistive force opposing the corrosion process when the effect of all physical factors limiting the supply of the depolarizing agent to the surface have been eliminated. If we denote this resistance by  $r$ , viz.

$$r = E/q_0 \dots \dots \dots (5)$$

We then have, for the net driving force available for maintaining the transport of depolarizing agent to the surface under attack when the specimen is corroding at a rate  $q$ ,

$$E - qr \text{ or } E(1 - q/q_0) \text{ volts.}$$

This is the factor with which we will be concerned in treating the more complicated phenomena concerned with transport processes involving forced and natural convection.

### SUMMARY.

The influence of the processes involving the transport of matter on the rate of corrosion has been studied by means of a circular disc protected by a guard-ring. This device reduced the geometrical nature of the flow of matter to one in a single dimension. The variation of the corrosion rate of such a surface was

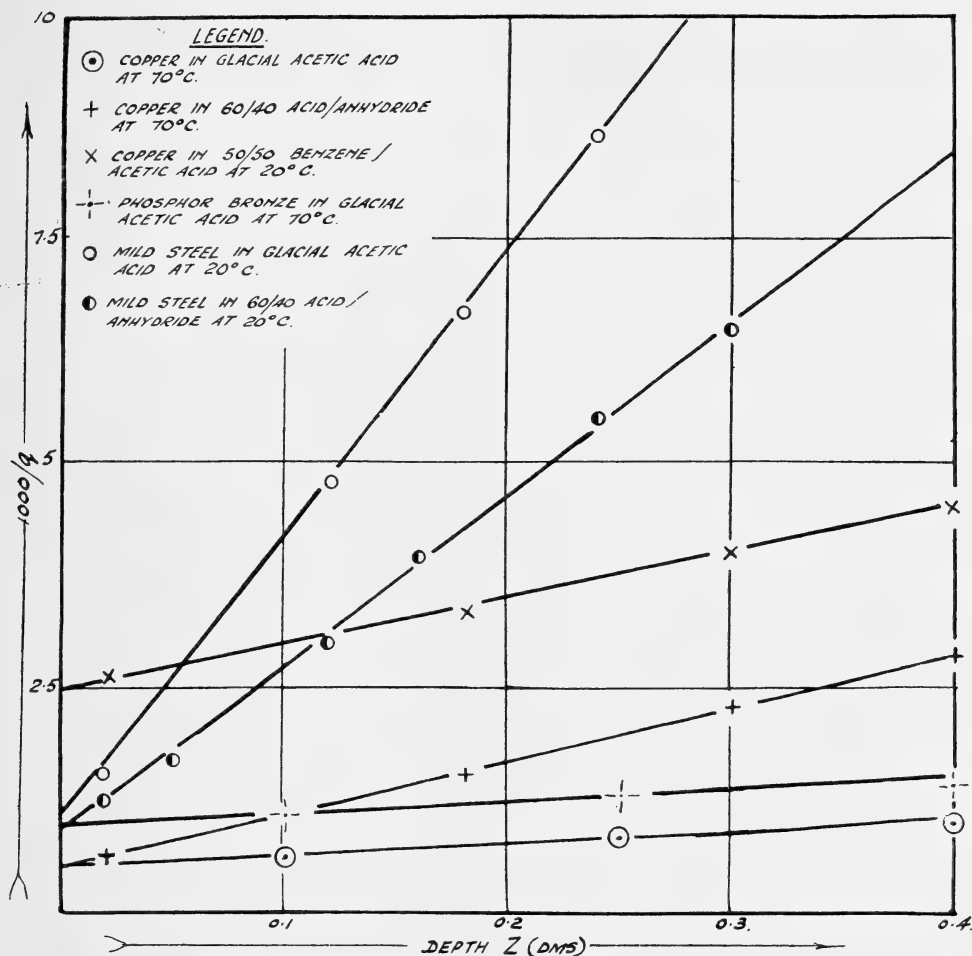


Fig. 4.

studied as a function of the orientation of the surface and shown to be a minimum when it faced upwards. It was concluded that convective transfer was absent under these conditions. The corrosion rate, from a horizontal surface facing upwards and protected by an electro-chemical guard-ring, was then studied as a function of the depth of immersion.

The systems studied included copper, copper alloys and steel in acetic acid, acetic anhydride mixtures. Experimental results plotted in the form : reciprocal

of the corrosion rate ( $1/q$ ) versus the depth ( $z$ ) of immersion give straight lines with positive intercepts on the  $1/q$  axis. These intercepts have been interpreted as a measure of the rate of corrosion under such conditions that the depolarizing agent (atmospheric oxygen) is made freely available at the surface. The slopes have been interpreted as a measure of the "conductivity" of the corrodant for the depolarizing agent, a factor which, it is suggested, would be of primary importance in the interpretation of the effect of convection of the rate of corrosion.

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# THE INFLUENCE OF FORCED CONVECTION ON THE PROCESS OF CORROSION.

By R. C. L. BOSWORTH, Ph.D., D.Sc., F.Inst.P.

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## INTRODUCTION.

That the phenomena occurring at the interface between a fluid electrolyte and an electrode, usually solid, can be influenced by the mechanism available for the transport of ions in the fluid has been recognized since the days of Nernst (1904). Nernst introduced the concept of a *diffusion layer* as that of a quiescent fluid zone of definite thickness across which matter may be transferred only by molecular conduction and in which no convection currents occur. The bulk of the fluid outside the diffusion layer is assumed to be so well stirred up by convection as to be effectively at uniform concentration. It then follows that the rate of transfer to the interface is governed by the product of the concentration difference across the diffusion layer, the diffusivity in the layer and the reciprocal of the thickness of the layer. Since the diffusivity is a specific property of the system concerned the diffusion layer thickness is the property which determines the influence of concentration difference on the rate of transfer.

The Nernst concept of a *diffusion layer* has been extended by Levich (1942, 1944, 1947) to that of a *diffusion boundary layer* defined by analogy with the boundary layers of hydrodynamics and of thermal convection. Agar (1947) has used this concept of a diffusion boundary layer treated as a Nernst diffusion layer in order to estimate the influence of the current density on overvoltage, and has applied his figures specifically to the deposition of iodine. His method is based on an assumed analogy between matter flow and heat flow both under conditions of natural convection and the final figures he obtains supports his initial assumptions. He makes no use of the analogy other than that of determining boundary layer thicknesses and associated properties.

In a series of measurements on the rate of transfer of metal ions from solid metal to liquid electrolyte—or measurements of the rate of corrosion of certain metals by acids—under such conditions that all convection currents could reasonably be presumed to have been eliminated, the author (Bosworth, 1949) was led to infer a possible analogy between corrosive matter loss and convective heat loss from a lagged hot body geometrically similar to the one undergoing corrosion. It is clear that if this analogy could further be developed it would yield information on other properties concerned in the transport of matter as well as the diffusion boundary layer thickness. This, and the succeeding paper, will describe attempts to study the behaviour of corroding bodies under regulated conditions of forced and natural convection by the same method as that which has proved so successful in heat transfer problems; namely by the use of dimensionless quantities analogous to the Nusselt, Prandtl, Peclet and Grashof numbers.

## THE TABLE OF ANALOGOUS PROPERTIES.

Table 1 below gives, on the left-hand side, a list of the properties and their units used in the treatment of forced and natural convection from a cylindrical

TABLE 1.

Thermal Properties.			Properties Connected with Corrosion.		
Property.	Symbol.	Unit.	Property.	Symbol.	Unit.
Heat Flux .. ..	$q$	calcs. cm. <sup>-2</sup> sec. <sup>-1</sup> .	Corrosion rate .. ..	$q$	mgrms. dm. <sup>-2</sup> day <sup>-1</sup> .
Temperature difference .. ..	$\theta$	° C.	Limiting corrosion rate .. ..	$q_0$	mgrms. dm. <sup>-2</sup> day <sup>-1</sup> .
Transmittance .. ..	$h$	calcs. cm. <sup>-2</sup> sec. <sup>-1</sup> ° C. <sup>-1</sup>	Effective cell e.m.f. . . .	$E(1 - q/q_0)$	volts.
Thermal conductivity .. ..	$k$	calcs. cm. <sup>-1</sup> sec. <sup>-1</sup> ° C. <sup>-1</sup> .	—	$\frac{q}{j/E}$	mgrms. dm. <sup>-2</sup> day <sup>-1</sup> volt <sup>-1</sup> .
Diameter of hot body .. ..	$d$	cms.	—	$\frac{E(1 - q/q_0)}{j/E}$	mgrms. dm. <sup>-1</sup> day <sup>-1</sup> volt <sup>-1</sup> .
Length of hot body .. ..	$l$	cms.	Diameter of corroding body	$d$	dms.
Mass rate of flow .. ..	$\gamma$	grms. sec. <sup>-1</sup> .	Length of corroding body	$l$	dms.
Viscosity .. ..	$\eta$	poises.	Mass rate of flow .. ..	$\gamma$	mgrms. day <sup>-1</sup> .
Acceleration due to gravity ..	$g(981)$	cms. sec. <sup>-2</sup>	Viscosity .. ..	$\eta$	mgrms. dm. <sup>-1</sup> day <sup>-1</sup> .
Heat capacity (Const. $p$ ) ..	$c_p$	calcs. grm. <sup>-1</sup> ° C. <sup>-1</sup> .	Acceleration due to gravity	$g(7.32.10^{11})$	dm. day <sup>-2</sup> .
Density .. ..	$\rho$	grms. cms. <sup>-3</sup> .	—	—	—
Quantity of heat per unit volume.	$c_p \rho \theta$	calcs. cm. <sup>-3</sup>	Density .. ..	$\rho$	mgrms. litre <sup>-1</sup> .
Volumetric heat capacity ..	$c_p \rho$	calcs. cm. <sup>-3</sup> ° C. <sup>-1</sup> .	Quantity of corrodant per unit volume.	$C$	mgrms. litre <sup>-1</sup> .
Coefficient of volumetric expansion .. ..	$\beta = \frac{1}{\rho} \frac{\partial \rho}{\partial \theta}$	° C. <sup>-1</sup> .	Quantity of corrodant per unit volume required to change $E$ by unity.	$K = \frac{\partial C}{\partial E}$	mgrms. litre <sup>-1</sup> volt <sup>-1</sup> .
Thermometric conductivity	$\kappa = \frac{k}{c_p \rho}$	cms. <sup>2</sup> sec. <sup>-1</sup> .	Diffusivity of corrodant ..	$D_c = \frac{j}{EK}$	dm. <sup>2</sup> day <sup>-1</sup> .

body. On the right-hand side the corresponding properties associated with the flow of the depolarizing agent to a corroding body are given with their units and suggested symbols. The units have been selected in such a way as to be consistent with the usual technical measurements of  $q$  (the rate of corrosion) in milligrammes decimetres<sup>-2</sup> days<sup>-1</sup> or  $8.64 \times 10^9$  C.G.S. units.  $E$  (the corrosion cell e.m.f.) in volts has been taken as defining the fourth fundamental unit in this system. The complete set of corrosion properties will thus be measured in decimetres, milligrammes, days and volts or in d.m.d.v. units.

Two new quantities are introduced in this table, namely  $K$  and  $\xi$ , the former defined by

$$K = \frac{\partial C}{\partial E} \dots\dots\dots (1)$$

and the latter by

$$\xi = \frac{\partial \rho}{\partial C} \dots\dots\dots (2)$$

$K$  is thus a measure of the capacity of the system for the corrodant, or the quantity in solution required to change the overall cell e.m.f. by one volt; and  $\xi$ , a dimensionless quantity, is defined as the change in density produced by unit change in the concentration of the corrodant. The diffusivity term  $D_c$  is simply defined by analogy with the thermometric conductivity or thermal diffusivity.

#### EXPERIMENTAL MEASUREMENTS ON FORCED CONVECTION.

In these experiments the body of the metal corroded took the form of a cylindrical tube, being part of a pipe system through which the corrodant flowed at a measured rate. The test piece fitted flush into glass pipes of the same diameter so that no eddies were created by any discontinuity in the rate or direction of flow. The test piece was weighed before and after a measured time interval during which the flow rate ( $\Gamma$ ) has been maintained constant. From a series of such measurements on any one tube,  $q$  could be measured as a function of  $\Gamma$ . Various tubes of copper, brass, phosphor bronze and mild steel of different lengths and diameters were used. The resultant  $q$  versus  $\Gamma$  curves were all of the same form. Very low rates of flow produced no increase in the rate of corrosion. Further increase in the flow rate resulted in a sharp increase in the rate of corrosion, but at still higher flow rates the rate of corrosion again became independent of the rate of flow. An increase in corrosion rate with flow rate has been recorded by Hatch and Rice (1945). In all the examples studied the velocity of flow required to give practically a stationary final corrosion rate were well within the region of laminar flow. Figure 1 gives some illustrative results obtained in the study of corrosion of a mild steel tube 10.0 cms. long and 0.33 cm. internal diameter, by a 60/40 acetic acid anhydride mixture; and Figure 2 similar results from a copper tube 15.6 cms. long and 0.454 cm. internal diameter, both at 20° C. The group of curves shown in Figure 3 refer to the corrosion of copper tubes of the various lengths and diameters indicated on the legend, exposed to a 50% aqueous acetic acid solution. The tubes were prepared from a given batch of copper and were given an identical heat treatment and finally quenched in alcohol just before use. The corrosion rates for very fast and very slow rates of flow were independent of the diameters of the tubes. At intermediate rates the shorter and finer tubes corroded relatively faster than the longer and wider ones.

#### THE PROBLEM OF HEAT LOSS UNDER FORCED CONVECTION.

The problem of the change in heat transmittance ( $h$ ) with change in the velocity of flow in a pipe has been subject to considerable study and experimental results have been co-ordinated by means of dimensionless quantities.

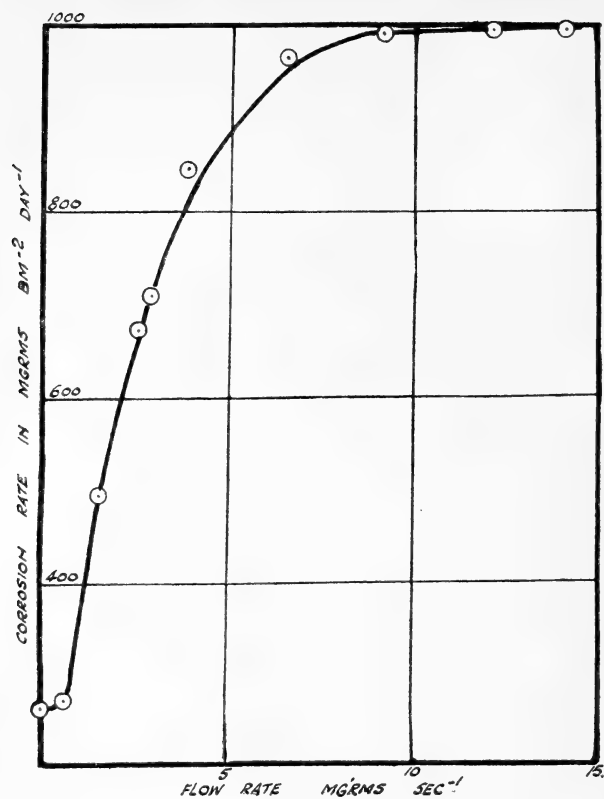


Fig. 1.

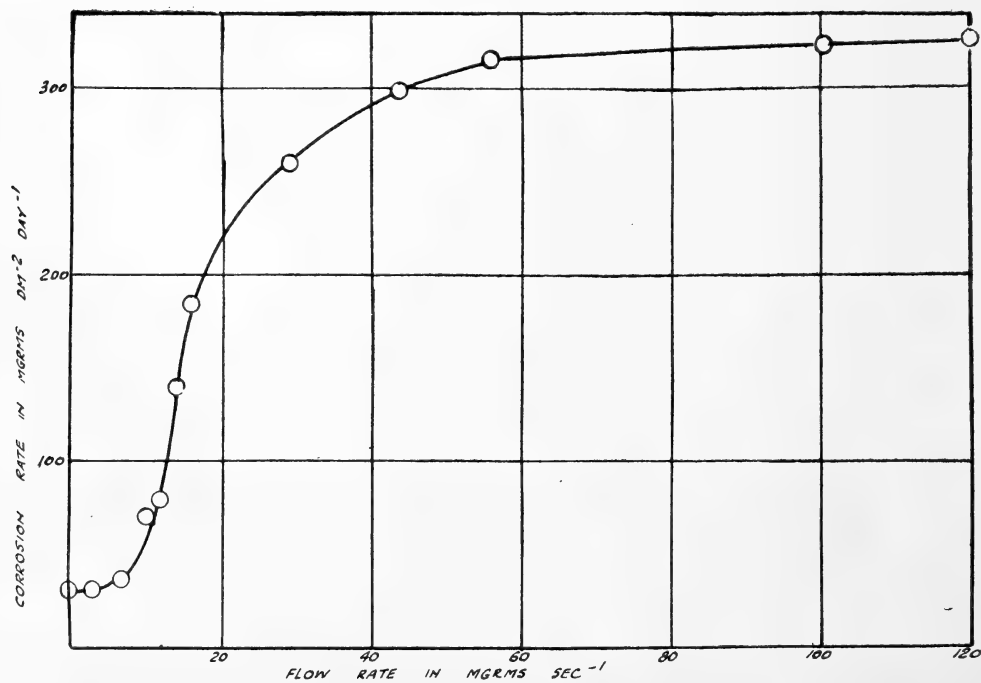


Fig. 2.

For heat transference in the region of laminar flow McAdams (1942) gives the expression

$$\frac{hd}{k_0} = 2.01 \left( \frac{\Gamma c_p}{kl} \right)^{1/3} \left( \frac{\eta}{\eta_w} \right)^{0.14}, \dots\dots\dots (3)$$

where  $\eta$  is the viscosity of the fluid in the centre of the pipe and  $\eta_w$  that at the

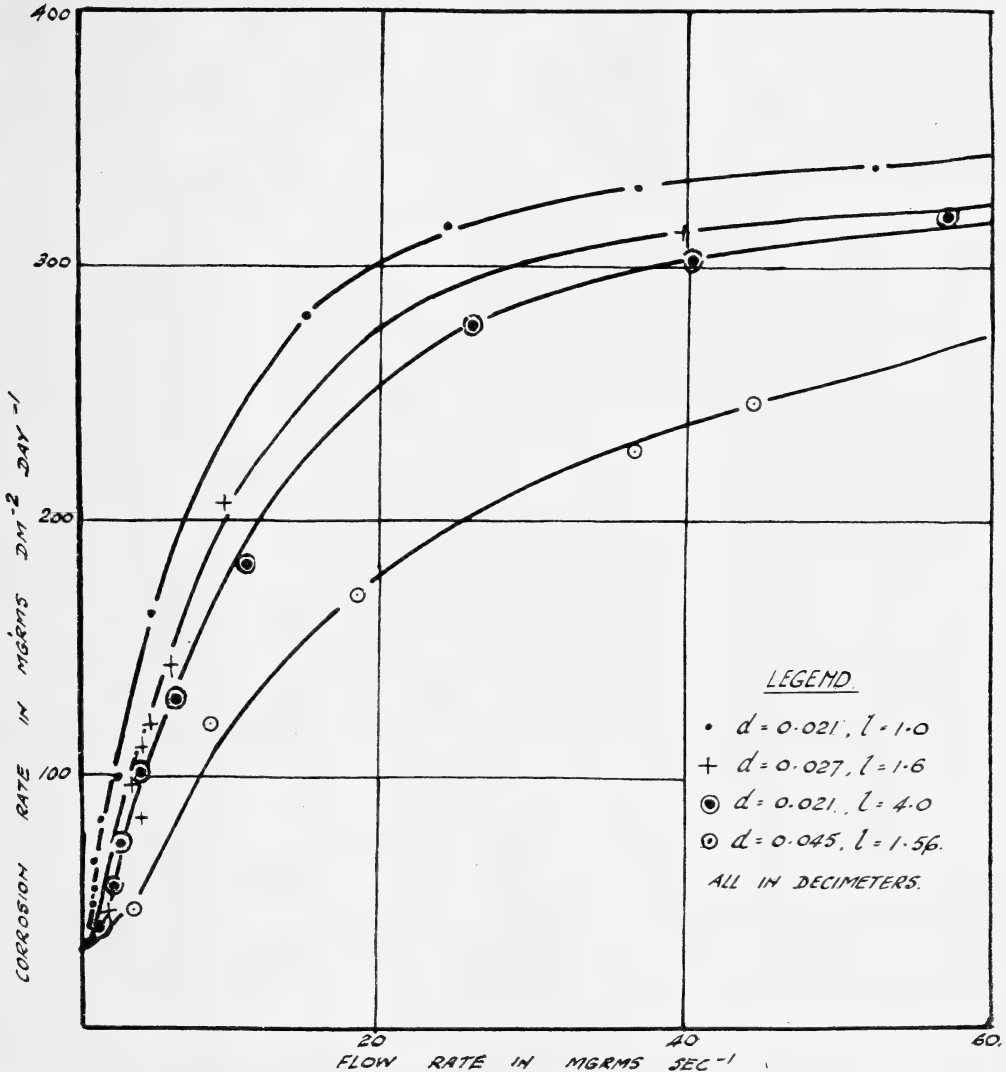


Fig. 3.

walls. The other symbols have the meanings outlined in Table 1. When convection is transporting not heat but the soluble products of corrosion there is no reason why the viscosity at the walls should be significantly different from that at the centre of the pipe. Equation (3) transposed to quantities concerned with corrosion will therefore take the form

$$\frac{qd}{j(1-q/q_0)} = 2.01 \left( \frac{\Gamma K}{jl\rho} \right)^{1/3} E^{1/3} \dots\dots\dots (4)$$

where the symbols again have the meanings given in Table 1. Equation (4) may be rewritten as

$$\frac{1}{q} - \frac{1}{q_0} = 0.498 \left( \frac{d^3 l}{\Gamma} \right)^{1/3} \left( \frac{\rho}{KEj^2} \right)^{1/3}$$

or

$$\frac{\partial \left( \frac{1}{q} \right)}{\partial \left( \frac{d^3 l}{\Gamma} \right)^{1/3}} = 0.498 \left( \frac{\rho}{KEj^2} \right)^{1/3} \dots \dots \dots (5)$$

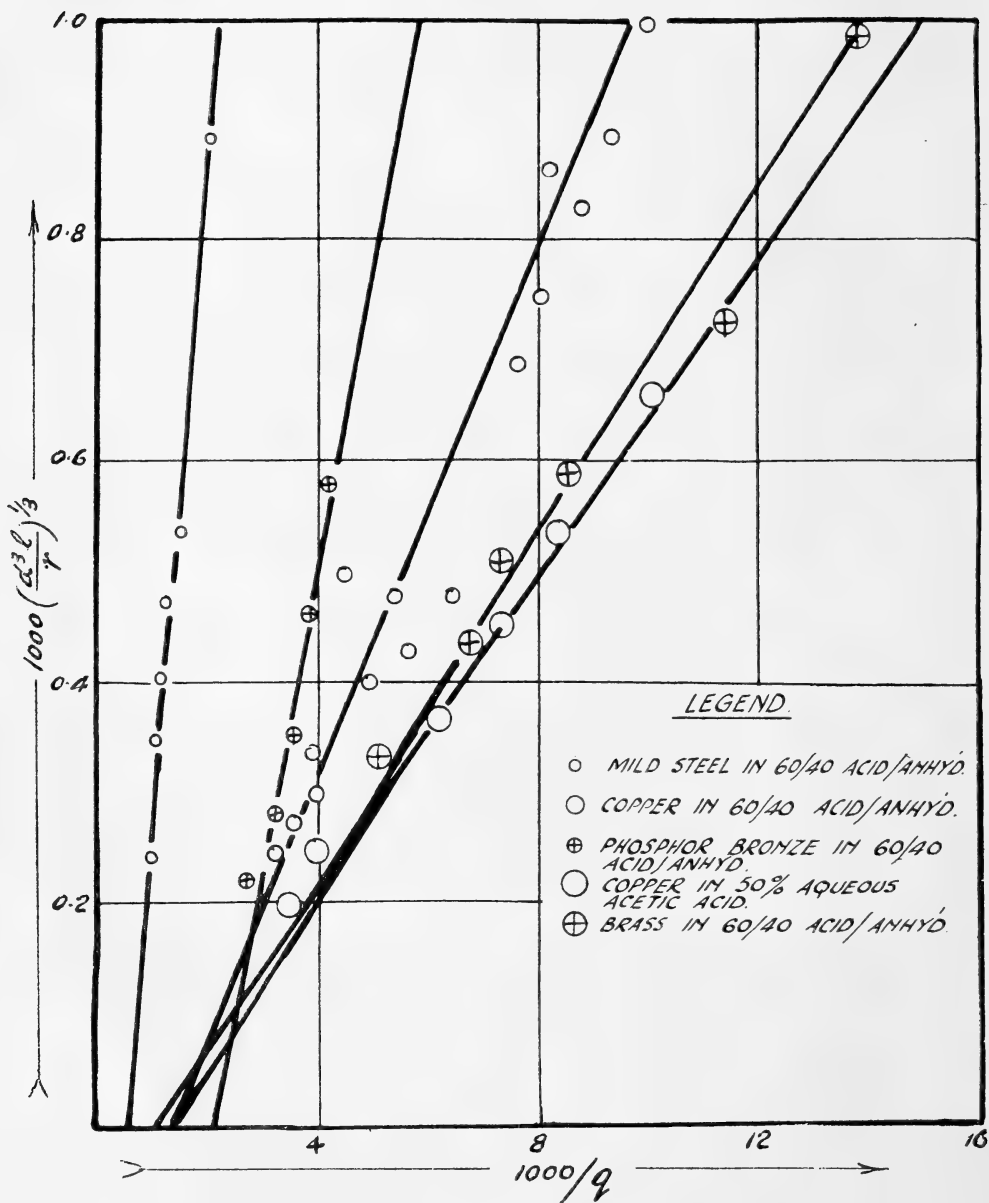


Fig. 4.

So that experimental results may therefore be fitted to this equation by plotting  $1/q$  versus  $\left(\frac{d^3 l}{\Gamma}\right)^{1/3}$ . The results treated in this way are shown in Figure 4.

The experimental points for each system studied lie on a straight line, giving a positive intercept on the  $1/q$  axis. The slopes of these lines are a measure of the

quantity  $\left(\frac{\rho}{KEj^2}\right)$ . Thus we have

$$\left(\frac{\rho}{KEj^2}\right)^{1/3} = 2.01 \frac{\partial\left(\frac{1}{q}\right)}{\partial\left(\frac{d^3 l}{\Gamma}\right)^{1/3}} \dots\dots\dots (5a)$$

=16.1 d.m.d.v. units (copper in 60/40 acetic acid-acetic anhydride).

=29.1 d.m.d.v. units (copper in 50% aqueous acetic).

=3.32 d.m.d.v. units (mild steel in 60/40 acetic acid-anhydride).

=7.44 d.m.d.v. units (phosphor bronze in 60/40 acetic acid-anhydride).

=26.1 d.m.d.v. units (brass in 60/40 acetic acid-anhydride).

The values of the densities  $\rho$  in d.m.d.v. units are :

$1.056 \times 10^6$  for 50% aqueous acetic acid and

$1.060 \times 10^6$  for 60/40 acetic acid acetic anhydride.

Using the values of  $j$  from the earlier paper, we may now compute the values of the product  $KE$  for the five examples above. An independent measurement of  $E$  (from over-voltage measurements or from the Gibbs' free energy of the corrosion reaction) is necessary before we can derive the values of the capacity terms  $K$ . However, for many purposes the product  $KE$  is all that is required. Thus the coefficient of diffusion  $D_c$  of the depolarizing agent is related to  $j$  and  $KE$  by the expression

$$D_c = \frac{j}{KE} \text{ decimetres}^2 \text{ day}^{-1}$$

$$= 1.16 \times 10^{-3} \frac{j}{KE} \text{ cms.}^2 \text{ sec.}^{-1}.$$

Values of  $KE$  and  $D_c$  computed from the figures above are given in Table 2.

TABLE 2.

Metal.	Corrodant.	$KE$ in d.m.d.v. Units.	$D_c$ in	
			d.m.d.v. Units.	C.G.S. Units.
Copper .. ..	50% aqueous acetic.	1.20	5.0	0.0058
Copper .. ..	60/40 acetic acid-acetic anhydride.	2.3	4.6	0.0053
Mild steel ..	60/40 acetic acid-acetic anhydride.	10.8	4.8	0.0056
Brass .. ..	60/40 acetic acid-acetic anhydride.	1.5	4.1	0.0048
Phosphor bronze	60/40 acetic acid-acetic anhydride.	4.2	4.3	0.0050

It will be observed from this table that whereas the values of  $KE$  vary practically over a tenfold range the values of the diffusivities are, within the limits of an experimental error accentuated by the act of cubing, constant. It therefore appears that these observations lend support to a suggestion that the same depolarizing agent is concerned in all these cases. The absolute magnitude of the diffusion coefficient is considerably higher than those usually given by liquid systems. Thus Sherwood (1937) claims that the diffusivities of most organic and inorganic matter in liquids lie between  $0.3$  and  $1.5 \times 10^{-5}$  cms.<sup>2</sup> sec.<sup>-1</sup>, or about  $3 \times 10^{-3}$  of the figures estimated above for the diffusivity of the depolarizing agent.

#### SUMMARY.

The rate of corrosion of metal tubes through which a corrodant liquid is caused to flow has been measured as a function of the rate of flow. The rate of corrosion increases as the flow rate increases but becomes practically stationary when the rate of flow is still quite low.

The variation of the rate of loss of matter with the rate of flow takes the same form as that for the rate of loss of heat from a geometrically similar lagged hot pipe through which a conducting fluid is caused to flow.

The diffusivity of the depolarizing agent, defined as an expression analogous to the thermometric conductivity, proves to be the same for all metals and corrodants studied, and is of the order  $5 \times 10^{-3}$  cms.<sup>2</sup> sec.<sup>-1</sup>.

A table is given showing the properties concerned in the convective loss of heat together with the corresponding terms involved in the convective transfer of matter concerned in the process of corrosion.

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# THE INFLUENCE OF NATURAL CONVECTION ON THE PROCESS OF CORROSION.

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## INTRODUCTION.

Two earlier papers (Bosworth, 1949*a*, 1949*b*) have traced a degree of parallelism between heat loss by conduction and convection and matter loss by corrosion under conditions of forced convection and in circumstances in which all convection currents have been eliminated by the use of guard rings. The present paper extends this study to the consideration of natural convective losses from cylindrical bodies placed horizontally in a corrodant liquid. The convective heat loss from cylindrical bodies such as hot wires or steam pipes immersed in fluids has, on account of its economic importance, been subject to very considerable detailed examination. A fairly complete review of the findings in this field have been given by Lander (1942). For convective heat loss from horizontal cylinders the emittance  $q$  is related to the other physical variables by means of the dimensionless equation

$$\frac{qd}{k\theta} = F\left(\frac{d^3 \rho^2 g}{\eta k} \frac{c_p}{\beta} \frac{\theta}{k}\right) \dots\dots\dots (1)$$

where the symbols have the meanings given in Table 1 of the previous paper (Bosworth, 1949*b*) and  $F( )$  is a function which has been determined experimentally.

The methods of correlating experimental data expressed by means of equation (1) have been extended by analogy with the problems of the convective loss of matter by evaporation. Thus Sutton (1934), Powell and Griffiths (1939) and Pasquill (1943) have shown that losses by evaporation follows laws analogous to the loss of heat from similarly shaped hot bodies. The convective loss by corrosion, in as much as the rate is controlled by the conveyance of the active constituent to the surface and the removal of the products of reaction by convective currents set up as a result of the density changes produced by the reaction, appears to be quite analogous to the convective loss of water by evaporation with the simple difference that the convective current now flows downwards past the corroding body. If we transpose equation (1) over to properties concerned with corrosion according to Table 1 of the previous paper (Bosworth, 1949*b*) we get

$$\frac{qd}{j(1-q/q_0)} = F\left(\frac{d^3 g \zeta K^2 E^2}{\eta j(1-q/q_0)}\right) \dots\dots\dots (2)$$

## EXPERIMENTAL.

The validity of equation (2) has been tested experimentally by placing a number of cylinders of different metals and different diameters in a horizontal position at a given depth (2 cms.) below the free surface of different corrodant liquids in such a way that the cylindrical and not the end faces could be attacked. After standing in a thermostat for a given time, ranging from 24 to 168 hours, the samples were removed and weighed and the corrosion rates ( $q$ ) determined. The metals investigated included deoxidized copper, mild steel, phosphor bronze and a brass (37% Zn, 63% Cu).

Of the various factors which occur in equation (2), the values of  $j$  (the corrosion conductivity) and  $q_0$  (the maximum corrosion rate) have been determined by experiments on the guard ring equipment (Bosworth, 1949a). The product  $KE$  has likewise been determined (for the systems studied) by measurements under conditions of forced convection (Bosworth, 1949b). Figures for  $\eta$ , the viscosity of the corrodant medium, are readily available, so that there remains only the quantity  $\xi$  to be determined before equation (2) may be put to an experimental test. This factor may be computed from observations of the density of the corrodant before and after a given quantity of each metal has been dissolved in a known volume. Samples of the corrodant were therefore collected after various measured masses of each metal had dissolved in a known volume and their densities were determined by pycnometer measurements in a constant temperature room.

### RESULTS.

The results obtained from the study of corrosion from horizontal cylinders are summarized in Figure 1, in which the corrosion rates for various metals, in each of a number of selected corrodants at 20° and 70°, are plotted against the

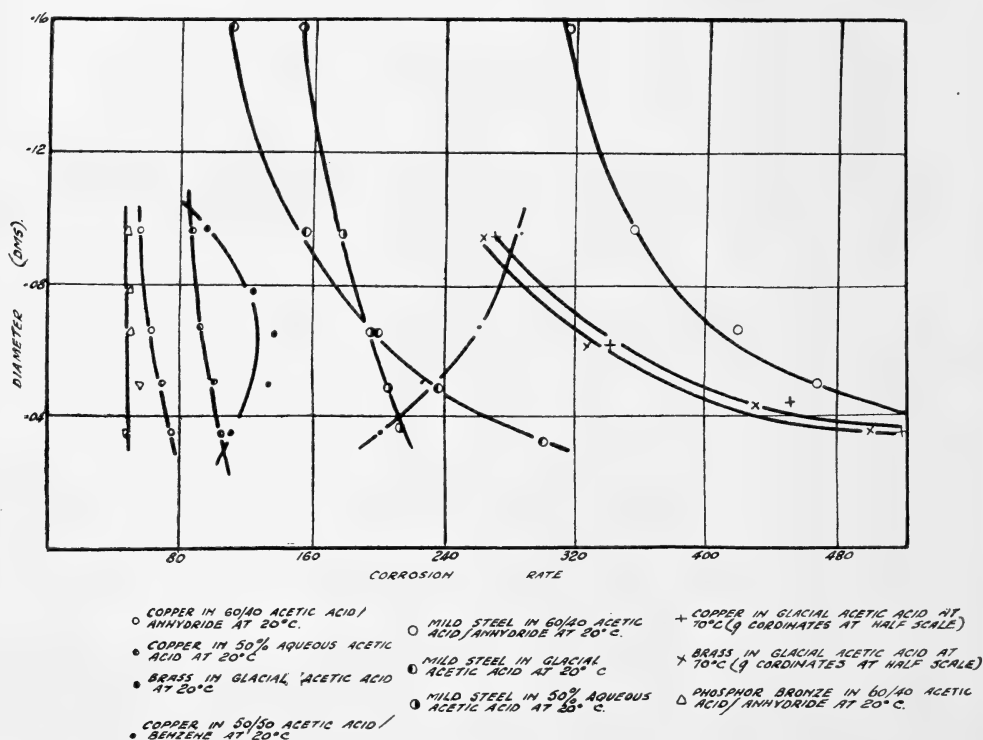


Fig. 1.

diameter of the specimen. In order to present as much data as possible on the one graph the scale for the  $q$  (or corrosion rate) axis referring to measurements at 70° C. is half that used for the measurements at 20° C.

It will be observed from the figure that for those systems in which the corrosive action is comparatively mild the rate of corrosion (in units of mass lost per unit area per unit time) varies only slightly with the diameter, and varies in such a way that the rate is somewhat faster for the smaller specimens. For

systems in which the corrosion rate is faster, such as mild steel at 20° C. or the copper alloys at 70° C., the variation of  $q$  with  $d$  (the diameter) is much more pronounced, so much so that for these systems the product  $qd$  (or the mass loss per unit length per unit time) is practically a constant. The one system examined with a very large value of  $j$  at room temperature (namely copper in 50% acetic acid 50% benzene) also gave a big variation of  $q$  with  $d$ , but one in the opposite direction, i.e. one in which the larger specimens corroded relatively faster than the smaller.

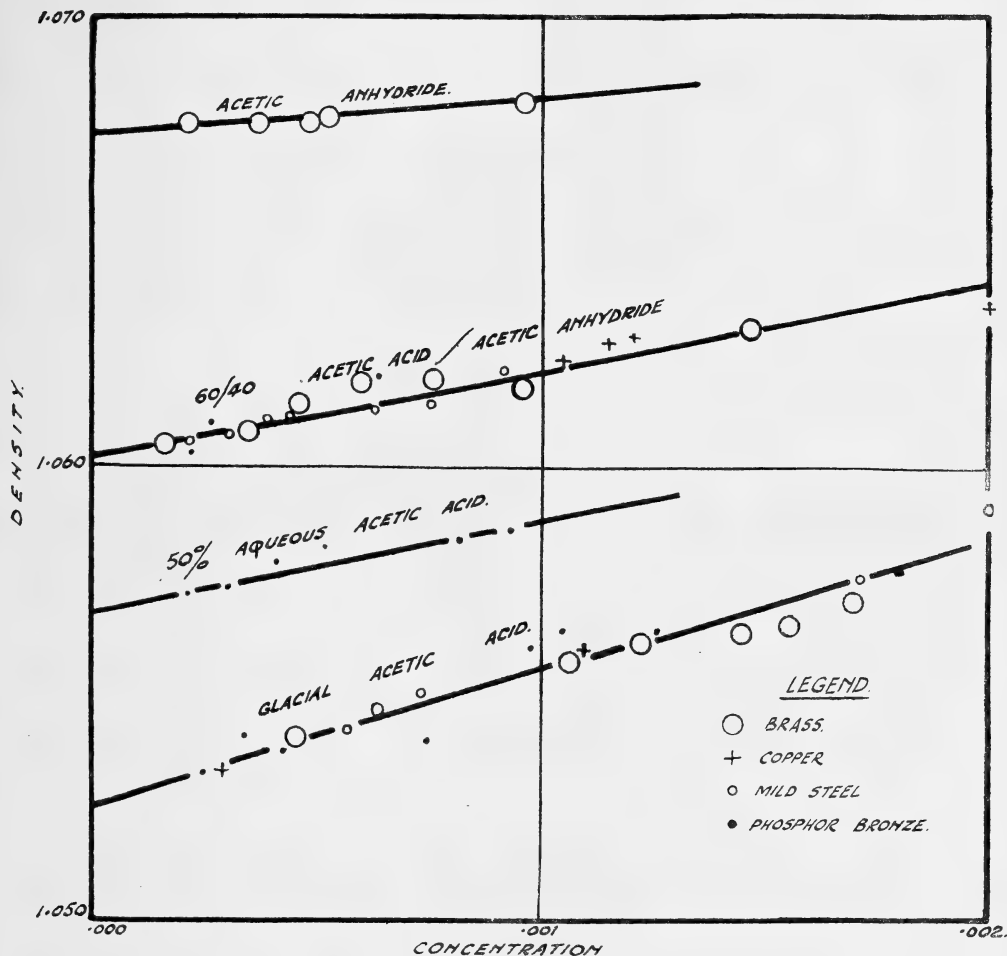
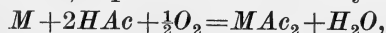


Fig. 2.

The dimensionless quantity  $\xi$  referred to above is defined as the ratio of the density change produced to the concentration of corroded metal measured in units of mass per unit volume of corrodant. While some water was formed during the corrosion action, represented chemically by



where  $M$  represents any divalent metal; the corrodants examined were hygroscopic in nature and care was necessary in order to prevent the condensation of additional water from the atmosphere with consequent dilution of the corrodant. Figure 2 shows densities plotted against the concentrations for some of the

systems studied. It will be seen that the different metals and alloys studied do not give significantly different results with respect to this property. The different fluids tested do however behave differently, the lower the density of the fluid the more pronounced the density change produced by dissolving a given small quantity of metal in it. The values of  $\xi$  from Figure 2, with the associated values of  $\rho$ , the original densities of the corrodants, are given in Table 1.

TABLE 1.

Corrodant.	Density $\rho$ .	$\xi$ .
Acetic anhydride .. ..	1.0674	0.7
60/40 acetic acid-acetic anhydride ..	1.0602	1.7
50% aqueous acetic acid .. ..	1.0568	2.0
Glacial acetic acid .. ..	1.0524	3.0
50/50 acetic acid-benzene .. ..	0.9475	12.0

#### CORRELATION OF RESULTS ON NATURAL CONVECTION.

We have now found, in the case of four of the systems studied, all the data necessary in order to compute the magnitude of both of the dimensionless quantities in equation (2). These systems are: copper in 50% aqueous acetic acid, and copper, mild steel, brass and bronze in the 60/40 acetic acid—acetic anhydride mixture. In Figure 3 the data for these systems, each represented by distinctive points, are shown plotted as

$$\log \frac{qd}{j(1-q/q_0)}$$

versus

$$\log \frac{d^3 g \xi K^2 E^2}{\eta j(1-q/q_0)}.$$

The full line shown on the figure is the curve for the corresponding dimensionless quantities involved in the loss of heat from horizontal cylinders by natural convection. This curve was taken from the paper by Lander (1942). The excellent agreement between the points, for the corrosive loss of matter by natural convection; and the curve, for the loss of heat from geometrically similar bodies by thermal convection, is a very clear indication that the phenomena involved are similar and the process which removes the products of corrosion from a surface and brings a continuous supply of the depolarizing agent is essentially the same as that involved in the removal of heat by the natural convection currents.

Data for correlation of all the curves shown on Figure 1 in terms of the dimensionless quantities shown in Figure 3 are not yet complete, mainly because sufficient independent values of  $KE$  are not available. However, if we assume that corrosion data would follow the heat convection curve over a wider range than shown above we may make certain interesting deductions the implications of which will be examined in a following paper. It has been shown that, for higher temperature corrosion, the product  $qd$  is practically a constant. In heat flow problems the corresponding quantity also becomes practically constant when the right-hand side of equation (1) is made less than about  $10^{-4}$  (Bosworth, 1944). We conclude, then, that the condition  $qd = \text{a constant}$  in a corrosion problem means that the right-hand side of equation (2) is very small. This might be effected, for example, by the value of  $K$  decreasing with increase in temperature, a fact which becomes significant when an attempt is made to interpret  $K$  in terms of the physical and chemical properties of the solution.

## CONCLUSIONS.

As a result of the study of mild steel and copper alloys in acetic acid and acetic anhydride mixtures under such physical conditions that the removal of the products of reaction from the corroding surface takes place in a closely defined manner, it is concluded that an analogy may be set up between the rate of matter loss by corrosion on the one hand and the rate of heat loss from a lagged hot body on the other. Further, when the physical variables concerned with each phenomena are expressed as dimensionless products corresponding to the Nusselt number and the product of the Grashof and the Prandtl numbers respectively, the same function expresses the relationship between the parallel sets of dimensionless products applying to both phenomena.

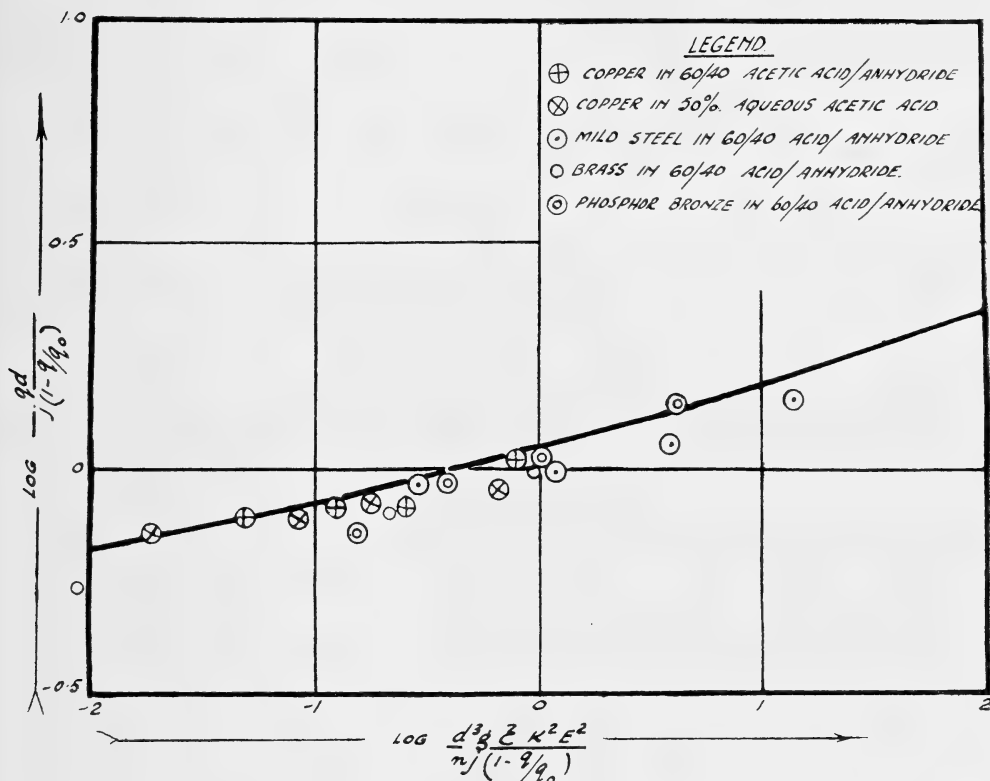


Fig. 3.

This result suggests that a method for estimating the behaviour of large-scale metal members subject to corrosion could be established by setting up an appropriate thermal model. However, it must be emphasized that the principles as developed in these three papers apply at the moment only to a restricted field of corrosion problems—namely to those in which bimetallic corrosion cells are absent and in which the products of corrosion do not form insoluble films and thus give rise to a type of restriction to the flow of matter, of which a counterpart is not realized in the convective flow of heat.

## SUMMARY.

The corrosive loss of matter from a metal cylinder immersed horizontally in a corrodant liquid at a constant temperature has been measured for a number

of specimens of different diameters. The metals investigated included mild steel, copper and various copper alloys; the liquids acetic acid and acetic anhydride mixtures. In most cases  $q$  (the corrosion rate) tends to increase as  $d$  (the diameter) is decreased and in some cases the product  $qd$  is practically constant.

When the dimensionless products of the properties involved in corrosion analogous to the Nusselt, Prandtl and Grashof numbers are set up, the functional relationship between them is shown to be the same as that applying to the convective loss of heat from geometrically similar bodies.

It is suggested, therefore, that under certain conditions the use of thermal models could be a useful tool in extrapolating corrosion data from small to large-scale equipment.

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# THE FORMATION OF MOBILE AND IMMOBILE FILMS OF OXYGEN ON TUNGSTEN.

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## INTRODUCTION.

The contact potential method of studying the properties of films on metal surfaces has been developed into a tool suitable for both electro-positive and electro-negative films (Bosworth and Rideal, 1937; Bosworth, 1945). Since the contact potential difference between a covered and a bare surface is an easily measurable index of the fraction ( $\theta$ ) of the surface covered, it can be used to record the changes in  $\theta$  which follow such surface processes as evaporation and condensation. This paper will be devoted to an application of the contact potential method to the study of the condensation of oxygen on tungsten.

An analysis by Roberts (1935, 1938) of the kinetics of adsorption with dissociation of a diatomic gas has shown that condensation proceeds far more slowly if the film formed is mobile than if the film formed is immobile, particularly when the interaction between the adsorbed atoms (or adatoms) is large. For the rate of change of  $\theta$  (with time) Roberts gave the expression

$$\frac{d\theta}{dt} = \frac{2}{n_s} \frac{\alpha_2 p_2}{\sqrt{2\pi m k T}} \varphi(\theta), \dots\dots\dots (1)$$

where  $n_s$  is the number of spaces per unit area available for adsorption.

$\alpha$  is the condensation coefficient.

$p$  is the pressure due to the molecules.

$m$  is the mass of a single (diatomic) molecule.

$k$  is the Boltzmann gas constant,

$T$  is the absolute temperature, and

$\varphi(\theta)$  is a function derived by Roberts.

For an immobile film the function  $\varphi(\theta)$  takes the form

$$\varphi(\theta) = 1 - 1.75\theta - 0.3215\theta^2 - 0.0833\theta^3 - 0.0175\theta^5) \dots\dots (2)$$

For a mobile film  $\varphi(\theta)$ , while practically the same as for the immobile film at low values of  $\theta$ , decreases much more rapidly as  $\theta$  increases and, over the higher values of  $\theta$ , assumes a value which depends on the interaction energy of the adatoms, being the smaller the higher this energy.

The fraction of the surface covered at which  $\varphi(\theta)_{\text{mobile}}$  becomes significantly less than the corresponding value of  $\varphi(\theta)_{\text{immobile}}$  depends on the lattice arrangement on the surface. If each adsorption space on the surface has four near neighbours the value of  $\theta$  at which the difference becomes significant is a little less than 0.5. If the adsorption space has six near neighbours, this value of  $\theta$  is just under 0.33.

Many of the adsorbed films for which the property of surface mobility has been studied have shown immobility at low temperatures and mobility at higher temperatures (Bosworth, 1942). Accordingly it was considered desirable to study the condensation of oxygen on tungsten over a range of temperatures. Any occurrence of appreciable surface migration in times of the order of the

interval between two successive collisions of a gaseous oxygen molecule at the same lattice point should mean a change in the kinetics of the condensation process at a temperature marking the inception of the surface migration. •

#### EXPERIMENTAL.

The apparatus used consisted of a tube for the measurement of contact potential differences of the type already described (Bosworth and Rideal, 1937). A sketch of the apparatus used has been given by Bosworth (1945*a*). In addition to the normal two crossed tungsten filaments the tube contained a barium oxide coated nickel filament which had been previously heated in an oxygen atmosphere in order to convert the coating into  $\text{BaO}_2$ . When all the parts had been assembled the tube was exhausted, using a two-stage mercury diffusion pump; and all the metal parts, with the exception of the  $\text{BaO}_2$  coated filament, were thoroughly outgassed. Sodium metal was then distilled into the vessel in order to produce a mirror on the glass walls, but not on the metal filaments, which were maintained hot during this process. The vessel was finally sealed off under vacuum.

Any desired oxygen pressure could now be maintained in the tube first by immersion in a liquid air bath and then by heating the  $\text{BaO}_2$  coated filament with a known current. This produced an evolution of oxygen at a fixed rate; and since every oxygen molecule striking the cooled walls was immobilized by the sodium film, this also resulted in a fixed oxygen pressure which could be varied at will by varying the heating current to the oxygen-emitting filament.

The current-temperature curves for the two cross filaments were obtained by measuring the current-resistance characteristics at temperatures below  $1000^\circ \text{K.}$ , and the current-brightness temperature curve (using an optical pyrometer) in the higher temperature range.

Contact potential differences were obtained by drawing the infr saturation curve from emitter filament to collector filament. The former was maintained at a fixed temperature of the order  $2500^\circ \text{K.}$ , while the latter was taken through a series of small external potential differences (from  $-2$  volts to  $+1$  volt) with respect to the central point of the hot filament. A string galvanometer with recording camera was used to follow rapid changes in the contact p.d. The method of working was as follows: A stable equilibrium film was allowed to build up on the collector filament and a series of snapshots of the galvanometer string taken with the camera, over a range of external applied potentials. A suitable external potential was then selected so that the expected curve for the variation of the emission with change in the contact potential difference consequent on a change in the chemical nature of the surface film should lie wholly within the range of the camera. The oxygen pressure was adjusted to the desired figure by means of the current through the barium dioxide source and the collector filament was heated to  $2200^\circ \text{C.}$  to clean it. The camera drive was then set going. The collector filament temperature was then dropped to the figure at which condensation was to be studied by suddenly changing the heating current. Initially rapid changes in galvanometer current occurred and the camera was stopped when this change became substantially constant. Further records were then obtained by reflash the collector filament and then dropping the temperature to some other point in the condensing range ( $90$  to  $1000^\circ \text{K.}$ ). As explained above, changes in the oxygen pressure could be effected by changing the heating current on the  $\text{BaO}_2$  source. The relative pressures attained could be measured from the slope of the initial part of the condensation curve or from the whole of the condensation curve at  $90^\circ \text{K.}$ , at which temperature condensation follows entirely the mechanism associated with the immobile film.



## EXPERIMENTAL RESULTS.

The results accruing from the various experimental runs were collected in the first instance in the form of records of the infrasaturation emission versus time curves for the various experimental conditions studied. Using the known current-volts characteristic of the assembly, the curves were first changed to contact p.d. versus time curves and then by means of the relationship between the contact p.d. and  $\theta$  found earlier for oxygen on tungsten films (Bosworth, 1945*b*) were finally converted to  $\theta$  versus time curves. Some illustrative curves of this nature are shown in Figures 1 and 2.

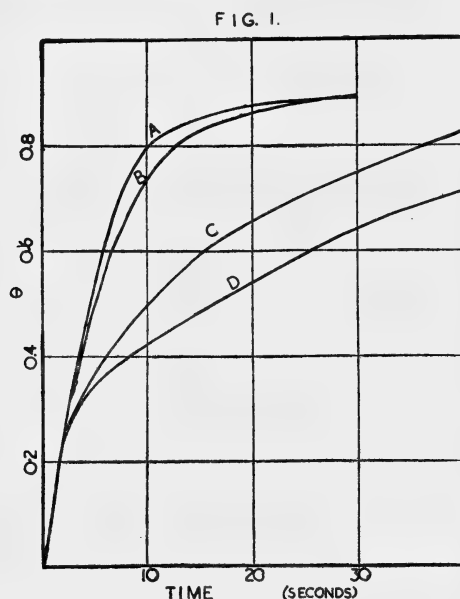


Figure 1 refers to condensation at a fixed oxygen pressure of  $1.1 \times 10^{-6}$  mms. of mercury and at a series of different temperatures. Curve A records the process of condensation at  $90^\circ \text{K.}$ , curve B condensation at  $540^\circ \text{K.}$ , curve C at  $690^\circ \text{K.}$ , and curve D at  $920^\circ \text{K.}$

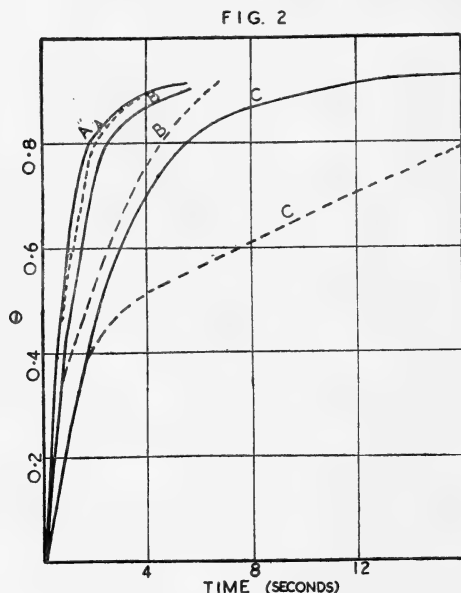
Figure 2 refers to condensation at a pair of fixed temperatures, one each in the mobile and the immobile range, and at a series of different oxygen pressures. Curves AA record condensation at a pressure of  $7.4 \times 10^{-6}$  mms. of mercury, curves BB at  $4.4 \times 10^{-6}$  mms., and curves CC at  $2.0 \times 10^{-6}$  mms. In each case the heavy lines refer to condensation at  $90^\circ \text{K.}$  and the broken lines to condensation at  $830^\circ \text{K.}$

It will be observed that at about  $\theta = 0.5$  or a little less the condensation proceeds the more slowly the higher the temperature at any fixed pressure, and more than proportionally slowly the lower the pressure at any fixed temperature. These results are not such as would be expected from the simple Roberts' theory.

## THEORY.

In the Roberts' theory for the condensation of a completely mobile film the condensation proceeds the more slowly the lower the quantity ( $\eta$ ) or  $e^{-V/kT}$ , in which  $V$  is the interaction energy between a pair of atoms on the surface.  $V$  varies only slowly with the temperature. Accordingly  $\eta$  is expected to increase with an increase in temperature. Condensation on a completely mobile film is

thus expected to proceed more rapidly at higher temperatures and this, as pointed out above, is not observed. However, a sudden onset of a mobility on the surface akin to a type of two-dimensional melting is also a phenomenon which has only been recorded in a few special cases. Much more usually the process of acquiring a state of surface mobility is more akin to a two-dimensional vaporization. On the picture given by Lennard Jones (1937) the mobile adatom is in a certain state of high energy and remains in that state for a finite time before being deactivated to return to the normal state of being fixed to a given lattice point. In this static condition the adatom remains, on the average, for a much longer time interval before being reactivated to the mobile condition. At any given instant the number of adatoms in the mobile state is only a small fraction of the total number. In considering the effect of activated mobility on the rate of condensation it would appear that the important factor is the probability of a given adsorbed atom migrating to a neighbouring lattice point before that point suffers a collision from a component atom of a gaseous molecule. Higher surface temperatures are associated with more frequent activations to the mobile state and therefore at such temperatures the film behaves as though it



were more completely mobile in the Roberts sense. Again at lower pressures the time intervals between successive collisions become longer, so that the film also behaves as though it were more mobile.

At any fixed temperature and pressure the rate of condensation of a (truly) mobile film depends on the quantity  $\eta$ .

$$\eta = e^{-V/kT},$$

where  $V$  is the interaction energy between a pair of adatoms. Above a value of  $\theta$  of about 0.5 the rate of condensation becomes practically zero when  $\eta$  is small. For oxygen on tungsten films we may estimate  $V$  from the figures given by Bosworth (1945) for the heat of evaporation of oxygen from nearly bare and from completely covered surfaces. These heats are respectively 154,000 and 66,000 calories per gramme molecule. Since each lattice point on the 110 surface plane has six almost equidistant neighbours, and further since dipole interaction as calculated by the Topping equation is negligible in comparison

with the total interaction, we may neglect all interaction other than that between near neighbours and write

$$V = \frac{154,000 - 66,000}{6} \\ = 14,700 \text{ calories per gramme molecule.}$$

For a temperature of  $750^\circ \text{K.}$ , therefore,

$$\eta \text{ becomes } 0.000068,$$

at which figure the value of  $\varphi(\theta)_{\text{mobile}}$  becomes very small in comparison with  $\varphi(\theta)_{\text{immobile}}$ .

We are now in a position to attempt a computation, from the observed rates of condensation, of a number of adatoms which become mobile in a given time. Let  $\left(\frac{d\theta}{dt}\right)_{\text{im.}}$  represent the rate of growth of the film calculated from the theory of immobile condensations for given conditions of  $\theta$ , temperature and external pressure and let  $\left(\frac{d\theta}{dt}\right)_{\text{obs.}}$  be the actual observed rate of growth under the given conditions. In addition to the variables which enter into the determination of  $\left(\frac{d\theta}{dt}\right)_{\text{im.}}$  the observed rate of condensation also depends on the state of distribution of the adatoms on the surface at the moment when further condensation takes place. This distribution of the adatoms on the surface may be characterized by two limiting states; a state  $\alpha$  in which every atom is attached at the point at which it made the initial collision with the surface and a state  $\beta$  in which surface spreading forces have attained equilibrium with thermal agitation. Condensation on a surface in state  $\alpha$  will proceed at the rate  $\left(\frac{d\theta}{dt}\right)_{\text{im.}}$ . Condensation on a surface in state  $\beta$  (provided  $\theta > 0.5$ ) will proceed at a rate which may be taken as negligibly small in comparison with  $\left(\frac{d\theta}{dt}\right)_{\text{im.}}$ . Surface migration results in a change from the state  $\alpha$  to the state  $\beta$ , and will be assumed to follow a "unimolecular" law, viz.

$$\frac{da}{dt} = -\kappa a$$

or

$$a = 1 - e^{-\kappa t_1}$$

where  $a$  represents the fraction of the covered surface in the state  $\alpha$ , and  $t_1$  is effectively the time elapsing between two successive collisions at two neighbouring lattice points on the surface. This time depends on the rate at which gaseous molecules impinge effectively on the surface. For immobile condensation the data of Roberts shows that the integral

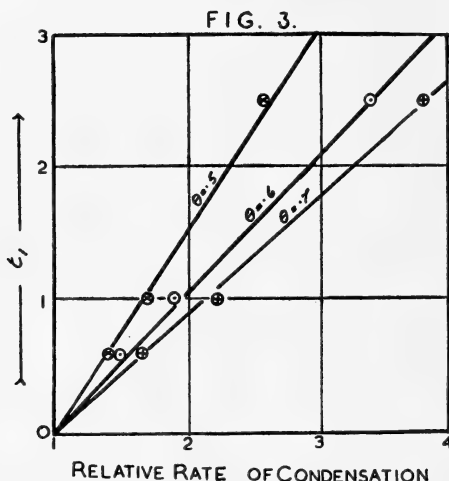
$$\int_0^\theta \frac{d\theta}{\varphi(\theta)}$$

attains the value of 1.0 at  $\theta = 0.52$ . Accordingly we take for  $t_1$  the time taken for the film to build up from zero concentration to  $\theta = 0.52$  under the given external conditions and with the film immobile, i.e. condensation at low temperature.

We may now write for the rate of condensation

$$\begin{aligned} \left(\frac{d\theta}{dt}\right)_{\text{obs.}} &= a \left(\frac{d\theta}{dt}\right)_{\text{im.}} \\ &= (1 - e^{-\kappa t_1}) \left(\frac{d\theta}{dt}\right)_{\text{im.}} \\ &\cong \kappa t_1 \left(\frac{d\theta}{dt}\right)_{\text{im.}}, \end{aligned}$$

so long as  $\left(\frac{d\theta}{dt}\right)_{\text{obs.}}$  is not of a different order of magnitude to  $\left(\frac{d\theta}{dt}\right)_{\text{im.}}$ . Thus



we have for the relative rates of condensation

$$\left(\frac{d\theta}{dt}\right)_{\text{obs.}} / \left(\frac{d\theta}{dt}\right)_{\text{im.}} = \kappa t_1.$$

The value of  $t_1$  may be read off from the curves shown on Figure 2 for the three different pressures employed. A plot of  $\left(\frac{d\theta}{dt}\right)_{\text{obs.}} / \left(\frac{d\theta}{dt}\right)_{\text{im.}}$  versus  $t_1$  is given in Figure 3 for the three different values of  $\theta$ , viz. 0.5, 0.6 and 0.7 at 830° K. These points fall on satisfactory straight lines passing through the origin. From the slopes the values of  $\kappa$  may be read off. The values thus obtained are:

- At  $\theta = 0.5$ ,  $T = 830^\circ \text{ K.}$ ,  $\kappa = 0.66$  reciprocal seconds.
- At  $\theta = 0.6$ ,  $T = 830^\circ \text{ K.}$ ,  $\kappa = 0.95$  reciprocal seconds.
- At  $\theta = 0.7$ ,  $T = 830^\circ \text{ K.}$ ,  $\kappa = 1.28$  reciprocal seconds.

#### CALCULATION OF THE DIFFUSION COEFFICIENTS.

The values of  $\kappa$  deduced above may be taken as measures of the times elapsing between successive activations of the same adatom to the mobile state, and thus may be related to the coefficients of surface diffusion ( $D$ ) by the expression

$$D = \frac{1}{2} \kappa \lambda^2,$$

where  $\lambda$  is the mean free path of the diffusing adatom and may be taken as the distance between two neighbouring points on the surface lattice. With the

high interaction energy characteristic of the oxygen on tungsten films it is unlikely that a mobile adatom will move over several lattice points before deactivation. Once it has moved out of the range of immediate neighbours of any other adatom it is practically in a uniform field. Thus we have for the diffusion coefficient of oxygen on tungsten

$$D = 3.7 \times 10^{-16} \kappa \text{ cms.}^2 \text{ sec.}^{-1}.$$

At  $830^\circ \text{ K.}$  the values of  $D$  are thus :

For  $\theta = 0.5$ ,  $D = 2.45 \times 10^{-16} \text{ cms.}^2 \text{ sec.}^{-1}$ .

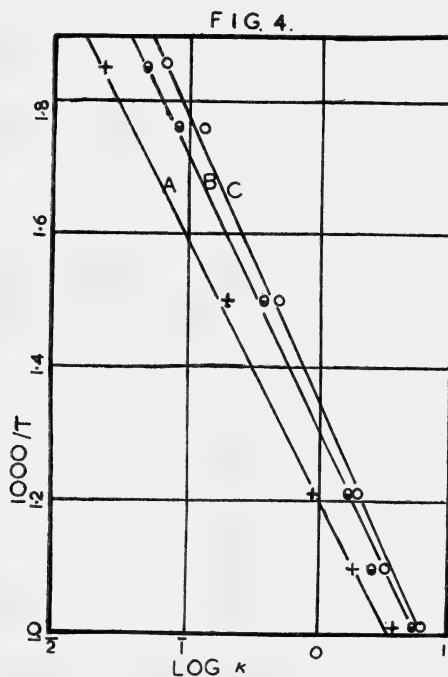
For  $\theta = 0.6$ ,  $D = 3.5 \times 10^{-16} \text{ cms.}^2 \text{ sec.}^{-1}$ , and

For  $\theta = 0.7$ ,  $D = 4.8 \times 10^{-16} \text{ cms.}^2 \text{ sec.}^{-1}$ .

From other measurements of  $\kappa$  it is possible to calculate  $D$  over a range of temperatures and values of  $\theta$ . For an activated process we expect  $D$  to vary with temperature according to a relation

$$D = D_0 e^{-b/T}$$

where  $D_0$  is a constant and  $b$  is a measure of the activation energy concerned. Some curves showing  $\log \kappa$  plotted against  $1000/T$  are given in Figure 4. Curve A



refers to  $\theta = 0.4$ , curve B to  $\theta = 0.5$ , and curve C to  $\theta = 0.6$ . Values of the activation energy computed from the slopes of these curves are :

For  $\theta = 0.4$ , activation energy 0.52 electron volts.

For  $\theta = 0.5$ , activation energy 0.50 electron volts.

For  $\theta = 0.6$ , activation energy 0.47 electron volts.

For  $\theta = 0.8$ , activation energy 0.46 electron volts.

These figures for the activation energy for surface migration are only a small fraction of the corresponding figures for the heats of vaporization for these same films.

## SUMMARY.

The contact potential difference has been used to study the condensation of oxygen on tungsten. At low temperatures the process follows the kinetics expected by the Roberts' theory of condensation with dissociation as an immobile film. At higher temperatures the condensation (once  $\theta$  has exceeded a value of about 0.4) proceeds the more slowly the higher the temperature or the lower the pressure. This is interpreted as due to the activation of some of the adsorbed oxygen atoms to a mobile state which proceeds the more rapidly the higher the temperature and the more completely the lower the pressure.

Calculation of the surface diffusion coefficient at 830° K. gives a figure of  $2.5 \times 10^{-16}$  cms.<sup>2</sup> sec.<sup>-1</sup> at  $\theta = 0.5$ , increasing with increase in  $\theta$  and an activation energy of 0.50 electron volts for  $\theta = 0.5$ , this time decreasing with increase in  $\theta$ .

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## A NOTE ON THE SIGMA PHENOMENON.

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### I. INTRODUCTION.

The sigma phenomenon, which has been described in some detail by Scott Blair (1938, 1944), is apparently of wide occurrence in the flow of semi-fluid pastes and slurries. In the method of studying the flow of such systems introduced by Schofield and Scott Blair (1930, 1931, 1935) we plot the mean velocity of the flow ( $U$ ) against the stress ( $\tau$ ) at the wall. If the one system is studied in a series of pipes of different diameters we get a series of straight lines, one for each tube diameter. Let us call the slope of these lines ( $dU/d\tau$ ) a quantity  $\sigma$ , and then proceed to plot  $\sigma$  against  $R$ , the radius of the tube. Were the fluid system studied to be Newtonian in behaviour, it would follow that the resultant plot would be a straight line passing through the origin and having a slope ( $d\sigma/dR$ ) equal to  $1/4 \eta$ , with  $\eta$  the viscosity. For systems exhibiting the sigma phenomenon the  $\sigma$  versus  $R$  plots are reasonable straight lines, but they do not pass through the origin, but instead give a positive slope  $\sigma_0$  on the  $\sigma$  axis. Thus for such systems we have

$$\frac{dU}{d\tau} = \sigma_0 + \frac{R}{4\eta} \dots\dots\dots (1)$$

In a paper by the author (Bosworth, 1947) it was shown that this equation had a form resembling that for the flow of a gas in a capillary at such a low pressure that slip flow was occurring, and it was further suggested that similar mechanisms for the transport of momentum from the fluid to the walls was operative. The peculiar properties of gas flow at low pressure are attributable to the fact that the carriers of momentum (viz. the moving molecules) travel through the system with mean free paths which are of the same order of size as the diameter of the tubes concerned. In seeking a similar mechanism for the transport of momentum in a semi-liquid slurry at atmospheric pressure it was suggested that the class of hypersonic longitudinal waves in the oscillatory motion into which the Debye theory of specific heats breaks up the thermal motion of condensed matter might contribute the momentum carriers with the long mean free paths. It will be the object of this paper to make an estimate of the magnitude of the sigma phenomenon in terms of the Debye distribution of frequencies. A similar estimate by the author (Bosworth, 1948) of the magnitude of the viscosity of normal liquids interpreted as a momentum transfer by transverse waves with mean free paths equal to the mean distance between two "holes" in the liquid has met with moderate success and will be used as a basis for the present calculation.

### II. DERIVATION OF THE INTENSITY OF THE MOMENTUM FLOW.

Following the practice adopted in the earlier papers we will refer to the stream of acoustical radiation as a stream of "phonons" carrying quanta of energy and momentum given by the quantum rule. The energy per unit volume

$dE$  associated with longitudinal waves of frequency lying between  $\nu$  and  $\nu + d\nu$  is given by

$$dE = \frac{4\pi\hbar}{c_1^3} \frac{\nu^3 d\nu}{e^{\hbar\nu/kT} - 1} \dots\dots\dots (2)$$

where  $c_1$  is the velocity of propagation of the longitudinal waves. The number of phonons  $dn_p$  per unit volume derived from longitudinal waves in the frequency range  $\nu$  to  $\nu + d\nu$  (or phonons of class B) is expressed by the relationship

$$dn_p = \frac{4\pi}{c_1^3} \frac{\nu^2 d\nu}{e^{\hbar\nu/kT} - 1} \dots\dots\dots (3)$$

The density of these same phonons ( $d\rho_p$ ) is likewise given by

$$d\rho_p = \frac{4\pi\hbar}{c_1^5} \frac{\nu^3 d\nu}{e^{\hbar\nu/kT} - 1} \dots\dots\dots (4)$$

While the number of phonons of class B striking unit area of the wall in unit time is

$$\frac{1}{4} dn_p c_1, \text{ or } \frac{\pi}{c_1^2} \frac{\nu^2 d\nu}{e^{\hbar\nu/kT} - 1}$$

A like number of phonons will leave the unit area of the wall in unit time in directions which are distributed according to the cosine law. A certain fraction

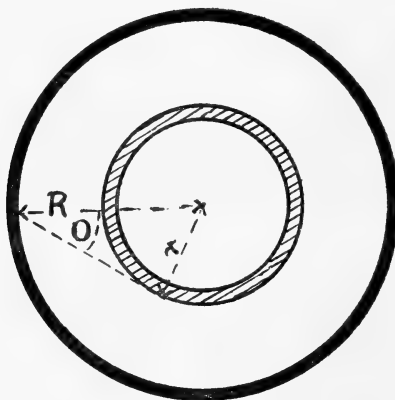


Fig. 1.

of that number will cross the surface of an inner cylinder of radius  $r$ . If  $R$  is the inner radius of the pipe (Figure 1) then phonons from any given point on the wall will cross the inner cylinder so long as they make an angle  $\theta$  with the normal which is less than  $\arcsin r/R$ , in a plane normal to the direction of flow.

The fraction crossing the inner cylinder is thus

$$\int_0^{\arcsin r/R} \frac{\sin \theta}{\cos \theta} d\theta = r/R.$$

If  $\alpha$  is the absorption coefficient the number of phonons in unit time and from unit wall area which are absorbed between the radii  $r$  and  $r - dr$  (the shaded area in Figure 1) is then

$$\frac{\pi}{c_1^2} \frac{\nu^2 d\nu}{e^{\hbar\nu/kT} - 1} \cdot \frac{r}{R} \cdot e^{-\alpha(R-r)} \alpha dr.$$



Let now  $u$  be the local velocity of flow of the zone of fluid represented by the shaded area. Generally  $u$  is a function of  $r$ . The momentum flow from unit area of the wall to an area  $r/R$  of the shaded zone and due to the phonons of class B now becomes

$$\frac{\pi}{c_1^4} \frac{u \hbar v^3 dv}{e \hbar v/kT - 1} \frac{r}{R} e^{-\alpha(R-r)} \alpha dr.$$

The total momentum flow to the shaded area carried by all the phonons arising from longitudinal waves thus becomes

$$\frac{\pi u r e^{-\alpha(R-r)} \alpha dr}{R c_1^4} \int_0^{\nu_0} \frac{\hbar v^3 dv}{e \hbar v/kT - 1} \dots\dots\dots (5)$$

where  $\nu_0$  is the limiting Debye frequency. For all temperatures considerably in excess of the Debye characteristic temperature  $\frac{\hbar \nu_0}{k}$  we may write approximately

$$e \hbar v/kT - 1 = \hbar v/kT,$$

so that expression (5) becomes

$$\frac{\pi r e^{-\alpha(R-r)} u k T \alpha dr}{R c_1^4} \frac{\nu_0^3}{3} \dots\dots\dots (6)$$

But now  $\nu_0$  is related to the number  $N$  of molecules in unit volume by

$$\nu_0^3 = \frac{9N}{4\pi} \frac{1}{\left( \frac{1}{c_1^3} \frac{2}{c_t^3} \right)}, \dots\dots\dots (7)$$

where  $c_t$  is the velocity of propagation of the transverse hypersonic waves. As in the earlier paper, we assume that the Cauchy-Poisson relation holds between  $c_1$  and  $c_t$ , namely that

$$5c_t^2 = 3c_1^2 \dots\dots\dots (8)$$

which on substitution in equation (7) gives

$$\nu_0^3 = 0.1886 \frac{9}{4\pi} N c_1^3 \dots\dots\dots (9)$$

and this, on substitution in expression (6), gives for the momentum transferred per unit time to the shaded area

$$0.1414 u e^{-\alpha(R-r)} \alpha dr \frac{r}{R} \frac{N k T}{c_1}.$$

This momentum flow yields a contribution ( $d\tau$ ) to the stress exerted by the fluid on the walls, namely

$$d\tau = 0.1414 \frac{u N k T}{c_1} \alpha e^{-\alpha(R-r)} dr \dots\dots\dots (10)$$

The total stress on the walls due to the longitudinal waves becomes

$$\tau = 0.1414 \frac{\alpha k T N}{c_1} \int_0^R u e^{-\alpha(R-r)} dr \dots\dots\dots (11)$$

Whenever sigma phenomena are in evidence there occurs considerable slip at the walls, thus  $u$  varies relatively slowly throughout the pipe except in the immediate vicinity of the walls. Under such conditions we may, without sensible error, take  $u$  outside the integral sign in equation (11) and replace it by  $U$ , the average velocity of flow in the pipe. Then we get

$$\tau = 0.1414 \frac{\alpha U N k T}{c_1} \int_0^R e^{-\alpha(R-r)} dr$$

$$= 0.1414 \frac{UNkT}{c_1} e^{-\alpha R} \dots\dots\dots (12)$$

as our final expression for the contribution to the stress on the wall due to the collision of photons originating from longitudinal waves.

### III. THE MAGNITUDE OF $\sigma_0$ .

On differentiation of equation (12) we obtain

$$\frac{dU}{d\tau} = \frac{7.07c_1}{NkT} e^{\alpha R} \dots\dots\dots (13)$$

Now from equation (1) we have for  $\sigma_0$

$$\begin{aligned} \sigma_0 &= \lim_{R \rightarrow 0} \frac{dU}{d\tau} \\ &= \frac{7.07c_1}{NkT} \end{aligned}$$

But since  $N$  is  $N/V$  where  $N$  is the Avogadro number and  $V$  is the molecular volume, and further since  $Nk$  is  $R$ , the ordinary gas constant, we get finally

$$\sigma_0 = 7.07 \frac{Vc_1}{RT} \dots\dots\dots (15)$$

For aqueous solutions  $c_1$  is of the order  $1.5 \times 10^5$  cms. sec.<sup>-1</sup> and at room temperature  $RT$  is  $2.5 \times 10^{10}$  ergs. Accordingly, for such solutions we have for  $\sigma_0$  the approximate value

$$\sigma_0 = 4.24 \times 10^{-5} V \text{ cms.}^3 \text{ secs.}^{-1} \text{ dynes}^{-1} \dots\dots\dots (16)$$

This estimated value of  $\sigma_0$  may be compared with the experimental values of Schofield and Scott Blair (1930) for various aqueous pastes. Such a comparison would enable  $V$ , the effective molecular volume of the pastes, to be computed. In the table below the experimental values of  $\sigma_0$  and the estimated values of  $V$  obtained therefrom are given in tabular form.

TABLE 1.  
*Effective Molecular Volumes Estimated from the Sigma Phenomenon.*  
(Data of Schofield and Scott Blair.)

Paste.	Percentage Solids.	$\sigma_0$ (cms. <sup>3</sup> sec. <sup>-1</sup> dynes <sup>-1</sup> ).	$V$ (Litres).
Clay .. ..	2.36	0.33	7.7
Kaolin .. ..	37.2	0.11	2.6
Plaster of Paris.. ..	5.8	0.017	0.40
Barytes .. ..	43.5	0.015	0.35
Subsoil .. ..	33.5	0.0055	0.13

These molecular volumes are very large and are more nearly appropriate to a gaseous rather than a liquid system. To the effusive transport of momentum resulting in the sigma phenomenon these slurries thus act as solutions which are very dilute on the molar basis.

### SUMMARY.

The suggestion that the sigma phenomenon observed in the flow of certain slurries is due to the transport of momentum to the walls by the acoustical vibrations into which the Debye theory resolves the thermal energy of the molecules is examined quantitatively. It is shown, subject to the assumptions

that the system is far above its Debye temperature and that the ratio of the velocities of the longitudinal and the transverse waves takes the Cauchy-Poisson value, that the value of  $\sigma_0$  is given by

$$\sigma_0 = 7.07 V c_1 / RT,$$

where  $c_1$  is the velocity of the longitudinal hypersonic waves and  $V$  is the effective molar volume of the slurry. Comparison of this equation with the measurements of Schofield and Scott Blair shows that  $V$  has a value of the order of a litre.

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## A NOTE ON THE ESSENTIAL OIL OF *BACKHOUSIA ANISATA* VICKERY AND THE OCCURRENCE OF ANETHOLE.

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Although specimens from the myrtaceous tree *Backhousia anisata* Vickery, indigenous to the north coast of New South Wales, were collected as long ago as 1910, it has been confused with *Eugenia ventenatii*, and its taxonomic position was not established until recently by Vickery (1941).

On account of the strong aniseed-like odour of the crushed foliage it has received the vernacular name of "Aniseed Tree", and this observation has prompted officers of the Forestry Commission of New South Wales to enquire into the economic value of the oil as a possible substitute for anise oil. This Institution has undertaken the examination of the oil obtainable from this species, and since a preliminary investigation shows promise of commercial value it has been decided to publish the results hitherto obtained. When further supplies of material become available, a more detailed examination of the oil will be made.

The examination so far shows that the foliage of this tree yields on steam-distillation 0.5% of a pale yellow oil strongly resembling anise oil of commerce in respect both to odour and taste. The principal component of the oil is anethole (*p*-propenyl anisole), present to the extent of about 60%, as compared with about 80% for anise oil. However, it is considered that by rectification or by freezing, a commercial equivalent of anise oil could be prepared, and would provide a local source of anethole. The oil of *B. anisata* is considered by the author to be far superior to fennel oil.

### EXPERIMENTAL.

Samples of foliage were supplied by the Forestry Commission of N.S.W. Two collections were made, one, received 4/7/46, from one restricted locality in the Bellenger River area of New South Wales; the other, received 11/11/46, was made up of foliage from three different and separated localities in the same area—Buffer Creek, Pine Creek and Kalang—the purpose of the second sample being to determine if the oil of this species is reasonably constant in composition to justify commercial exploitation.

Both samples consisted of leaves and terminal branchlets cut as for commercial distillation, and on steam-distillation they both yielded 0.5% of a pale yellow mobile oil, lighter than water and having a sweet taste and pronounced anethole-like odour. The oil froze readily to a crystalline mass on cooling in ice-water. The oils had the characteristics shown in the following table; figures for the British Pharmacopoeia specification for anise oil being given for comparison.

#### *Preparation and Characterization of the Anethole.*

Essential oil of *B. anisata* (47 g.) was frozen by cooling to about +5°. The crystalline mass was transferred to a chilled porous tile and pressed. By repetition of this process, 24 g. of white

	4/7/46 Sample.	11/11/46 Sample.	1932 B.P. Specifications. (Anise Oil).
Specific gravity at 20°/15·5° ..	0·9826	0·9806	0·980 to 0·994
Refractive index, at 20° .. ..	1·5535	1·5489	1·553 to 1·560
Optical rotation, 100 mm. tube ..	-1·15°	-1·88°	-2° to +1°
Freezing point .. .. .	14·5°	12·0°	Not below 15°
Melting point .. .. .	15·2°	13·2°	Not below 17°
Solubility in 90% V/V alcohol ..	Soluble in 1 vol.	Soluble in 1 vol.	Not more than 3 vols.
Ester number, mg. KOH per gramme	—	15·4	—
Ester number, mg. KOH/g, after acetylation .. .. .	—	87·6	—

crystals were obtained, melting at 21°–22° to a colourless oil of powerful anethole odour and taste, and having the following characters:

$d_{15}^{15}$	..	..	..	..	0·9912
$n_D^{20}$	..	..	..	..	1·5613
$\alpha_D$	..	..	..	..	inactive.

On oxidation of a portion with potassium permanganate by the procedure of King and Murch (1925), an excellent yield of a *solid acid* (neutral equivalent, 152) crystallizing in needles from hot water, and melting at 183–184° (uncorr.), was obtained. The melting point was not depressed by mixing with an authentic specimen of *anisic acid* (neutral equivalent, 152 (calculated)).

A further portion of the material was oxidized by the method of Shoesmith (1923) and a pale yellow liquid of aubépin odour resulted. It yielded a *p*-nitrophenylhydrazone m.p. 161·5° (uncorr.) undepressed by admixture with *p*-anisaldehyde *p*-nitrophenylhydrazone.

It is therefore concluded that the compound is *anethole*.

#### ACKNOWLEDGEMENTS.

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The Museum of Technology and  
Applied Science,  
Sydney.

# NITROGEN IN OIL SHALE AND SHALE OIL.

## VIII. THE DETECTION OF TAR BASES.

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### INTRODUCTION.

In connection with other aspects of this work it became necessary to develop an unambiguous test for the detection of tar bases in crude shale oil and its products.

The tar bases present in shale oil are principally pyridine homologues, though weakly basic pyrrole homologues are also present (Mapstone, 1948). Crude shale oil also contains a large proportion of non-basic nitrogenous compounds of unknown composition (Mapstone, 1949), but these were not of importance in the work described here. Tests carried out on the oil could indicate the presence of either pyridine homologues or of pyrroles, while tests on an acid extract of the oil would be mainly indicative of the pyridine bases because of the very low acid solubility of the pyrroles.

With strongly coloured samples, it was necessary to extract the bases with acid before applying the tests. A number of different tests were therefore examined for sensitivity for the detection of tar bases in solution in the lighter oils and in solution in dilute sulphuric acid as they were extracted from the darker coloured oils.

### SAMPLES TESTED.

The tar bases present in the acid sludge from the treatment of cracked shale gasoline were considered to be sufficiently representative of those initially present in the gasoline to be used for this work. They were therefore isolated as described previously (Mapstone, 1947) and purified by distillation. They contained 8.69% of nitrogen by weight, and the bases present would be almost entirely pyridine homologues.

Since preliminary work indicated the probable presence of approximately 5 p.p.m. of tar bases in refined shale gasoline, another suitable tar base-free hydrocarbon solvent was required for the determination of the sensitivity of the various reagents. The highly purified *n*-heptane-isooctane blend used for the determination of the octane rating of motor fuels was found to give a negative test with all except a few of the reagents used. In the cases where a positive result was obtained the reaction could be attributed to other factors. A 1% solution of the bases in the heptane-octane mixture (hereafter referred to as gasoline) was carefully prepared and the more dilute solutions prepared from it by dilution with further gasoline.

A solution of the purified bases in dilute sulphuric acid was prepared by dissolving 1.0 ml. of the bases in 250 ml. of 0.097 N sulphuric acid. Titration of portion of the solution showed that the excess acid was 0.0637 N, giving an 0.0333 N solution of the bases. This solution was diluted with further portions of the 0.0970 N acid to give the more dilute solutions required.

The light recycle oil (boiling range 5% at 360° F., 95% at 520° F) from the thermal cracking of crude shale oil is dark brown in colour, and it was therefore

necessary to extract the bases for detection. From the method of extraction and the boiling range the bases would be principally pyridine homologues together with any quinoline homologues that may be present. Fifty millilitres of the oil were washed with 200 ml. of 0.1061 N sulphuric acid. Titration of portion of the solution thus obtained showed that the excess acid was 0.0362 N, giving an 0.0699 N solution of the bases. This was diluted with further portion of the 0.1 N acid to give the more dilute solutions required.

With crude shale oil it was even more necessary than with the light recycle oil to extract the bases before detection. In the manner described for the light oil a 0.042 N solution of the bases from the crude shale oil was obtained in 0.1 N sulphuric acid.

Unless otherwise mentioned the tests on the hydrocarbon samples were carried out by adding two drops of the reagent to 5 ml. of the sample, and the tests on the acid extracts by adding four drops of the reagent to 1 ml. of the sample.

#### REAGENTS.

In deciding which reagents were to be tested, those which reacted with pyridine or quinoline or their homologues to give precipitates or developed colours were chosen. Since many alkaloids contain pyridine nuclei several "alkaloid" reagents were included. However, those alkaloid reagents which are based on concentrated sulphuric acid (e.g. Froehde's, Mandelin's and Erdmann's reagents) were not examined because of the action of the acid on the olefines in the gasoline samples, and with the samples dissolved in dilute acid, the dilution of the reagent would render them ineffective.

From the nature of their reaction with the tar bases the reagents were somewhat arbitrarily subdivided into seven classes which are discussed in turn.

##### (1) *Metal salts which precipitate the metal hydroxide.*

Pyridine and quinoline and their homologues are tertiary amines and their aqueous solutions can be sufficiently alkaline to precipitate the hydroxides from the solutions of the salts of various metals (Perkin, 1935). The sensitivity of the tests with such reagents would therefore depend principally on the solubility of the hydroxide of the metal, and the ease with which it could be seen when precipitated. The reagents were prepared by adding dilute ammonia dropwise to the aqueous solution of the metal salt until a slight permanent precipitate was formed. The reagent solution was used after filtration.

Five per cent. solutions of ferric chloride, cobalt nitrate, nickel nitrate, cupric nitrate and zinc chloride and a saturated solution of potassium alum were prepared in this manner. Another mixed reagent was prepared by the addition of 3 ml. of 1% ammonium aurine tricarboxylate solution to approximately 80 ml. of the saturated alum solution. A slight red precipitate was formed and removed by filtration. It was thought that the dye would be adsorbed on any aluminium hydroxide precipitate and render it more visible and thus possibly increase the sensitivity of the alum reagent.

On carrying out the test on samples with higher tar base concentrations a precipitate was thrown down but, with the limiting concentrations a film was formed at the gasoline-reagent interface. If an excess of reagent was used (e.g. 2 ml. per 5 ml. sample) the cobalt and aluminium reagents gave positive results even in the absence of tar bases. It was therefore necessary to adhere strictly to the test conditions in order to obtain reproducible results. The sensitivities of these reagents are presented in Table 1.

TABLE 1.  
Sensitivities of Reagents.  
Metal Salts which Precipitate the Metal Hydroxides.

Reagent.	Colour of Precipitate.	Sensitivity. <sup>1</sup>
Ferric chloride .. .. .	Red to yellow.	0.0001%.
Cobalt nitrate .. .. .	Pink.	Beyond 0.00005%.
Nickel nitrate .. .. .	Green.	0.0001%.
Cupric nitrate .. .. .	Green-blue.	Beyond 0.00005%.
Zinc chloride .. .. .	White.	Beyond 0.00005%.
Potassium alum .. .. .	White.	0.001%.
Alum plus ammonium aurine tricarboxylate .. .. .	Reddish.	0.001%.

<sup>1</sup> Sensitivity is quoted as the least percentage of tar bases (8.7% N) by volume which gave a positive test.

Because the reaction between these reagents and the tar bases involves the precipitation of the acid soluble hydroxides of the metals, they were applicable to the detection of only the free bases and could not be applied to the acid extracts.

(2) *Acids which precipitate insoluble salts of the bases.*

This group of reagents includes many which have been used for the separation, isolation and identification of tar bases, and several "alkaloid" reagents. Because of their varied nature they are discussed separately. The sensitivities of the reagents are presented in Table 2.

TABLE 2.  
Sensitivities of Reagents.  
Acids which Precipitate Insoluble Salts of the Bases.

Source of Bases.	Gasoline.		Light Oil.	Crude Oil.
Base dissolved in acid ..	Gasoline	0.1 N H <sub>2</sub> SO <sub>4</sub> .	0.1 N H <sub>2</sub> SO <sub>4</sub> .	0.1 N H <sub>2</sub> SO <sub>4</sub> .
Chlorplatinic .. .. .	0.1%	Nil	Nil	0.0001 N
Chlorauric .. .. .	0.05%	Nil	0.00007 N	0.00003 N
HCl in ether .. .. .	0.00005%	—	—	—
HCl (concentrated) .. ..	0.005%	—	—	—
Picric .. .. .	0.001%	Nil	0.02 N	0.0012 N
Styphnic .. .. .	0.1%	Nil	0.015 N	0.0002 N
Trinitro- <i>m</i> -cresol .. ..	0.05%	Nil	0.015 N	0.0002 N
Oxalic .. .. .	0.01%	—	—	—
Tannic .. .. .	0.2%	Nil	0.03 N	0.003 N
Phosphomolybdic .. ..	0.0005%	Nil	Nil	0.0002 N
Phosphotungstic .. ..	0.05%	0.003 N	0.00007 N	0.0002 N
Silicotungstic .. .. .	0.005% p.p.pt. 0.00005% colour	Nil	Nil	0.002 N

The sensitivities are quoted as percentage of tar bases (8.7% N) by volume in the gasoline solution, and as normalities in the dilute sulphuric acid solutions.

(a) *Chlorplatinic Acid.* This reagent precipitates the sparingly soluble platinichlorides of the bases and has been used extensively for this purpose. It is of interest that the earliest recorded isolation and separation of the tar



bases from shale oil involved the precipitation of the bases as their platini-chlorides which were separated by fractional crystallization (Williams, 1854, 1855). The reagent was prepared by dissolving 0.0942 gm. of platinum in aqua regia, evaporating the solution to dryness on a water bath, dissolving in 2 ml. of hydrochloric acid and making up to 20 ml. with distilled water. A positive test was indicated by the formation of a yellow-brown precipitate.

(b) *Chlorauric Acid*. This reagent is sometimes used to give sparingly soluble amine salts for the separation or identification of tar bases. It was prepared by dissolving 0.1998 gm. of pure gold in aqua regia, evaporating the solution to dryness on a water bath, dissolving in 2 ml. hydrochloric acid and making up to 20 ml. with distilled water. A positive test was indicated by the formation of a yellow-brown precipitate.

(c) *Hydrogen Chloride in Ether*. Since the hydrochlorides of the tar bases are insoluble in hydrocarbon solvents, the addition of hydrochloric acid should precipitate the chlorides, and as the precipitate would be soluble in water the sensitivity of the test should be increased by the use of an etherial solution of hydrogen chloride. The reagent was prepared by saturating redistilled ether with hydrogen chloride gas. A positive test was indicated by a yellowish or white cloudiness in the sample. An excess of reagent gave a positive test in the absence of tar bases. This test was suitable for hydrocarbon samples only.

(d) *Hydrochloric Acid (Concentrated)*. This test was based on the considerations outlined in (c) above, but since it was an aqueous reagent it was not expected to be quite as sensitive. However, the reagent is always readily available and was therefore included for comparison. A positive result was indicated by a white cloudiness in the sample.

(e) *Picric Acid*. This reagent is frequently used for the isolation, separation and identification of basic organic compounds. The reagent was used in the form of the saturated aqueous solution. A positive result was indicated by the formation of a yellow precipitate or a yellow film at the gasoline-reagent interface.

(f) *Styphnic Acid*. This reagent is frequently used instead of picric acid for the same purposes and gives similar results which are no doubt due to the similarity of structure (styphnic acid is 3-hydroxy picric acid). The test was carried out as with picric acid and gave similar results.

(g) *Trinitro m-cresol*. This reagent (3-methyl picric acid) was included for comparison. The test was carried out as with picric acid and gave similar results.

(h) *Oxalic Acid*. The oxalates of pyridine homologues have sometimes been used for their separation and identification. The reagent was used as a saturated aqueous solution. A positive result was indicated by a white precipitate or film.

(i) *Tannic Acid*. This reagent is commonly employed as an "alkaloid" reagent, and was therefore included in this series of tests. This reagent was used as a 10% aqueous solution. The formation of a brown precipitate indicated a positive result.

(j) *Phosphomolybdic Acid*. This "alkaloid" reagent was prepared by the method of Hawke and Bergeim (1937). A positive result was indicated by the formation of a precipitate which was brown in higher concentrations and white in the lower concentrations. An excess of reagent gave a white precipitate even in the absences of the bases.

(k) *Phosphotungstic Acid*. This "alkaloid" reagent was prepared by the method of Hawke and Bergeim (1937). The test was carried out by adding two drops of the reagent to 5 ml. of the sample. A positive result was indicated by

the formation of a precipitate the colour of which increased from orange-yellow to white with decreasing tar base concentration.

(l) *Silicotungstic Acid*. This "alkaloid" reagent was prepared by dissolving 2 gm. of sodium tungstate in 10 ml. of hot water, adding 5 ml. of syrupy sodium silicate solution (s.g. 1.7), acidifying with 2 N nitric acid, diluting with 100 ml. of water, boiling and filtering. The clear filtrate was then acidified with 5 ml. of concentrated nitric acid. The tests were carried out using twice the usual proportion of the reagent. A positive test was indicated by the formation of a light brown precipitate or, in greater dilution, a pink colour in the gasoline sample.

(3) *Alkali salts which precipitate a salt of the base.*

(a) *Potassium Ferrocyanide*. This reagent is used for the detection of pyridine (Perkin, 1935) because of the low solubility of pyridine ferrocyanide. The reagent was used in the form of a saturated aqueous solution. A positive result was indicated by the formation of a white precipitate with the lower boiling bases to deep brown precipitate with the higher boiling bases.

(b) *Potassium Dichromate*. This reagent is commonly used for the detection of quinoline (Perkin, 1935) because of the sparing solubility of quinoline dichromate. The reagent was used in the form of a saturated aqueous solution. A positive result was indicated by the formation of a yellow-orange to dark brown precipitate, the colour increasing with boiling point of the bases.

(c) *Potassium Triiodide*. This "alkaloid" reagent was prepared by dissolving 2 gm. of iodine and 4 gm. of potassium iodide in 100 ml. of water. A positive result was indicated by the formation of a brown precipitate.

The results of these tests are presented in Table 3.

TABLE 3.  
*Sensitivities of Reagents.*

- (a) Salts which precipitate a salt of the Base.  
(b) Reagents which precipitate a double salt of the Base.  
(c) Miscellaneous.

Source of Bases.	Gasoline.		Light Oil.	Crude Oil.
	Gasoline.	0.1 N H <sub>2</sub> SO <sub>4</sub> .	0.1 N H <sub>2</sub> SO <sub>4</sub> .	0.1 N H <sub>2</sub> SO <sub>4</sub> .
Bases dissolved in .. ..				
Reagent :				
Potassium ferrocyanide ..	0.5%	Nil	0.03 N	0.005 N
Potassium dichromate ..	0.01%	Nil	0.03 N	0.004 N
Potassium triiodide ..	0.05%	0.001 N	0.00001 N	0.0001 N
Mercuric chloride ..	0.05%	Nil	0.03 N	0.0002 N
Mayer's reagent ..	0.0005%	0.003 N	0.0007 N	0.0008 N
Dragendorff's reagent ..	0.00005%	0.0002 N	0.00001 N	0.0002 N
Sodium hydroxide ..	—	0.015 N	0.0035 N	0.0002 N
Nessler's reagent ..	0.001%	0.003 N	0.00002 N	0.000002 N

The sensitivities are quoted as percentage of tar bases (8.7% N) by volume in the gasoline solution, and as normalities in the dilute sulphuric acid solutions.

(4) *Reagents which give an insoluble double salt of the bases.*

The reagents discussed in this section could be classified in the previous section as the distinction is one of degree rather than type. The results are therefore presented with them in Table 3.

(a) *Mercuric Chloride*. With this reagent pyridine and quinoline and their homologues form complex mercurichlorides, usually of the form (BHCl)<sub>2</sub>HgCl<sub>2</sub>

but frequently the precipitated compound is more complex, e.g. 2·5 dimethyl pyridine gives the compound  $C_7H_9N \cdot HCl \cdot 6HgCl_2$  (Garrett and Smythe, 1902). The reagent was used in the form of a saturated aqueous solution. The formation of a precipitate indicated a positive result. With the lower boiling bases the precipitate was white, but it was more orange-brown with the crude oil bases.

(b) *Potassium Mercuric Iodide (Mayer's Reagent)*. This "alkaloid" reagent was prepared by dissolving 2·7 gm. of mercuric chloride and 10·0 gm. of potassium iodide in 190 ml. of water. A positive test was indicated by the formation of a precipitate, the colour of which was usually brown but, when near the limiting concentration of bases, was sometimes light brown, cream or even white.

(c) *Potassium Bismuth Iodide (Dragendorff's or Thresh's Reagent)*. This "alkaloid" reagent was prepared by the method outlined by Perkin (1935). A positive test was indicated by the formation of a red-orange precipitate, though the colour sometimes varied to red or brown.

#### (5) *Reagents which open the pyridine ring.*

The reagents discussed in this section cause the opening of the pyridine ring to give glutaconic aldehyde which forms brightly coloured Schiff's bases with primary aromatic amines.

(a) *Thionyl Chloride*. Pyridine can be converted into 4-pyridyl pyridinium chloride on heating with thionyl chloride and on treatment with alkali, this gives glutaconic aldehyde and 4-aminopyridine. Feigl and Anger (1939) developed a test which they reported to be sensitive to five  $\gamma$  of pyridine with a concentration limit of 1 : 10,000 by condensing the glutaconic aldehyde with  $\alpha$ -naphthylamine. All attempts to apply this test even to the pure shale tar bases or to pure pyridine yielded negative results.

(b) *Cyanogen Halides*. Cyanogen halides react with pyridine to give the unstable *N*-cyano-pyridinium halide which is readily hydrolysed to glutaconic aldehyde. This reaction has been applied to the colorimetric determination of traces of cyanides (Epstein, 1947) as well as pyridine (Barta, 1935) and the detection of alkaloids containing a pyridine ring (Shmuk, 1940, 1942). In this work the three cyanogen halides were tested and the product reacted with a saturated aqueous solution of aniline or a 1% alcoholic solution of *p*-nitro-aniline, anthranilic acid, or  $\alpha$ - or  $\beta$ -naphthylamine. The mixture was acidified and the colour change noted. The cyanogen chloride solution was prepared by adding 5 ml. of a 1% chloramine T solution to 2 ml. of a 1 N potassium cyanide solution. The cyanogen bromide and iodide solutions were prepared by adding bromine water or the potassium triiodide solution respectively to a 1 N potassium cyanide solution until there was a slight excess of the free halogen; this was removed by the addition of a few drops of the cyanide solution. The test was carried out by shaking 5 ml. of the sample with 1 ml. of the cyanogen halide solution followed by the addition of 1 ml. of the amine solution. After the colour had been noted concentrated hydrochloric acid was added dropwise until no further change occurred. With the cyanogen chloride and bromide the tests were satisfactory, but iodine was precipitated on acidification of the tests with cyanogen iodide. The results are presented in Table 4.

#### (6) *Salts which give co-ordination compounds with pyridine.*

Pyridine is noted for the large number of co-ordination complexes which it forms with metallic salts, but in order that such compounds may be used for the detection of pyridine or its homologues, they should either be insoluble in or extractable from the reaction medium, and should be preferably strongly

TABLE 4.  
Sensitivities of Reagents.  
Cyanogen Halides and Aromatic Amines.

Source of Bases.	Gasoline.		Light Oil.	Crude Oil.
Bases dissolved in .. ..	Gasoline	0.1 N H <sub>2</sub> SO <sub>4</sub>	0.1 N H <sub>2</sub> SO <sub>4</sub>	0.1 N H <sub>2</sub> SO <sub>4</sub>
A. Cyanogen chloride with—				
Aniline :				
Test .. ..	y. to r.br.	wh. to c.	wh. to c.	y. to c.
Sensitivity .. ..	0.75%	0.003 N	0.000001 N	0.000004 N
<i>p</i> -Nitro-aniline :				
Test .. ..	y. to or.	y. to c.	y. to c.	y. to c.
Sensitivity .. ..	0.75%	0.015 N	0.000003 N	0.00001 N
Anthranilic acid :				
Test .. ..	y. to r.br.	wh. to c.	wh. to c.	y. to c.
Sensitivity .. ..	0.75%	0.002 N	0.000001 N	0.000002 N
$\alpha$ -Naphthylamine :				
Test .. ..	lt.y. to r.br.	p. to c.	y. to c.	y. to c.
Sensitivity .. ..	0.75%	0.003 N	0.000001 N	0.000002 N
$\beta$ -Naphthylamine :				
Test .. ..	y.br. to br.	m. to c.	w. to y.	br. to lt.br.
Sensitivity .. ..	0.00005%	0.016 N	0.006 N	0.00002 N
B. Cyanogen bromide with—				
Aniline :				
Test .. ..	y. to r.br.	Nil	cr. to c.	cr. to c.
Sensitivity .. ..	0.75%	—	0.00003 N	0.00004 N
<i>p</i> -Nitro-aniline :				
Test .. ..	y. to r.br.	y. to c.	y. to c.	cr. to c.
Sensitivity .. ..	0.25%	0.003 N	0.00003 N	0.00002 N
Anthranilic acid :				
Test .. ..	y. to r.br.	y. to r.br.	y. to c.	cr. to c.
Sensitivity .. ..	0.75%	0.016 N	0.000015 N	0.00003 N
$\alpha$ -Naphthylamine :				
Test .. ..	br. to r.br.	cr. to c.	cr. to c.	cr. to c.
Sensitivity .. ..	0.75%	0.0013 N	0.00003 N	0.00004 N
$\beta$ -Naphthylamine :				
Test .. ..	br. to lt.br.	y.br. to br.	y. to lt.y.	br. to lt.br.
Sensitivity .. ..	0.00005%	0.016 N	0.0003 N	0.00004 N

The sensitivities are quoted as percentages of tar bases (10% N) in the gasoline sample, and as normalities in the diluted acid solutions.

Key :

br. = brown.  
c. = colourless.  
cl. = clear.  
cr. = creamy.

m. = milky.  
p. = pink.  
r. = red.  
wh. = white.

y. = yellow.  
or. = orange.  
lt. = light.

coloured. A preliminary survey suggested that the acetates, thiocyanates and cyanates of cobalt, nickel and copper were worth investigation as they were coloured and could be extracted from the aqueous solution by chloroform (Morton, 1946). The results are presented in Table 5.

(*a-c*) *Acetates*. Since the acetates of cobalt, nickel and copper are soluble in water, and the complexes are soluble in chloroform as well as water, they could be extracted satisfactorily from the acid solutions of the bases once formed. A preliminary examination indicated that the complex was stable and could be extracted from the aqueous solution only if the pH was greater than 4. The acetate reagent was therefore prepared to act as a buffer solution as well as to provide acetate ions by dissolving 15 gm. of sodium acetate crystals and 20 ml. of glacial acetic acid in sufficient water to give 100 ml. of solution. The test was

TABLE 5.  
Sensitivities of Reagents.  
Co-ordination Complexes with Salts.

Source of Bases. Salt :	Gasoline.		Light Oil.	Crude Oil.
	Gasoline	0.1 N H <sub>2</sub> SO <sub>4</sub>	0.1 N H <sub>2</sub> SO <sub>4</sub>	0.1 N H <sub>2</sub> SO <sub>4</sub>
Bases dissolved in .. ..	Gasoline	0.1 N H <sub>2</sub> SO <sub>4</sub>	0.1 N H <sub>2</sub> SO <sub>4</sub>	0.1 N H <sub>2</sub> SO <sub>4</sub>
Cupric acetate .. ..	—	0.00025 N	0.00007 N	0.00025 N
Cobalt acetate .. ..	—	0.00025 N	0.00015 N	0.00005 N
Nickel acetate .. ..	—	0.0005 N	0.0003 N	0.00025 N
Cupric thiocyanate .. ..	1.0%	0.003 N	0.002 N	0.002 N
Cobalt thiocyanate .. ..	0.1%	0.007 N	0.0008 N	0.004 N
Nickel thiocyanate .. ..	0.1%	0.003 N	0.0009 N	0.004 N
Cupric carbamate (?) .. ..	—	0.001 N	0.002 N	0.0003 N
Cobalt carbamate (?) .. ..	—	0.0005 N	0.0001 N	0.0001 N
Nickel carbamate (?) .. ..	—	0.001 N	0.003 N	0.0005 N

The sensitivities are quoted as percentage of tar bases (8.7% N) by volume in the gasoline solution, and as normalities in the dilute sulphuric acid solutions.

carried out by adding 1 ml. of this acetate reagent and 0.5 ml. of a 5% solution of the cobalt, nickel or cupric nitrate, and 1 ml. of chloroform, to 5 ml. of the solution of the tar bases in dilute sulphuric acid. The mixture was shaken and allowed to stand when the development of an amber colour in the chloroform layer indicated a positive test.

With pyridine the cupric acetate complex was green, but with the shale tar bases it was amber. This was first thought to be due to some impurity in the reagent but was later found to be due to the difference in the bases themselves. For comparison the tests were carried out using some pyridine which had been carefully freed from all homologues by refluxing with permanganate, and different boiling fraction of mixtures of pyridine homologues. The lower boiling homologues were obtained by fractionating denaturant grade pyridine (from coal tar) through a 12 pear column and the higher boiling fractions were obtained in previous work (Mapstone, 1947) by the careful fractionation of the shale tar bases through a 36-inch Fenske column at high reflux.

The results obtained are presented in Table 6, and indicate that the boiling range of the bases influence the colour of the complex formed. The tests were carried out on solutions containing two drops of the bases in 5 ml. of 0.1 N sulphuric acid.

Although pyridine gives complexes with salts of substituted acetic acids and its homologues (Morton, 1946 ; Reitzenstein, 1902, 1940), they were not included as it was felt that they would have little advantage, if any, over the acetates.

(d) *Cupric Thiocyanate.* The formation of a precipitate,  $\text{Cu}(\text{CNS})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ , which is soluble in chloroform to give an emerald green solution, is reported to be sensitive to 0.05% of pyridine (Morton, 1946 ; Spacu, 1922, 1923). In this work the test was carried out by adding two drops of a solution of 5 gm. of potassium thiocyanate in 10 ml. of water and two drops of a 0.5% solution of cupric nitrate to 5 ml. of the sample. This gave a black to greenish black precipitate of cupric thiocyanate. With the acid solutions the complex was extracted by the addition of 2 ml. of chloroform. A positive result was indicated by a green colour in the chloroform. With the acid samples containing the tar bases from gasoline the chloroform coagulated the dark green cupric thiocyanate precipitate and gave a yellowish-white precipitate at the interface. With the gasoline solution of the bases the black precipitate of cupric thiocyanate interfered with the observation of any colour. In this case the precipitate was

TABLE 6.  
Effect of Boiling Point of Bases on Colour of Acetate Complex.

Base.	Colour of Complex in Chloroform.		
	Cobalt.	Nickel.	Cupric.
Pure pyridine .. .. .	Amber.	Yellow-green.	Green.
Coal tar bases to 117° C. ..	Light yellow.	Light yellow.	Green-lemon.
"    "    117-133° C. ..	"	"	Light green.
"    "    133-145° C. ..	"	"	Light yellow.
"    "    145-155° C. ..	"	"	Lemon-green.
Shale tar bases 164-170° C. ..	Very pale bluish green.	Very pale bluish green.	Very pale bluish green.
"    "    170-180° C. ..	Yellowish green.	Yellowish green.	Yellowish green.
"    "    180-190° C. ..	Yellowish green.	Yellowish green.	Yellowish green.
"    "    190-200° C. ..	Yellow.	Yellow.	Yellow.
"    "    200-210° C. ..	Yellow.	Yellow.	Yellow.
"    "    210-212° C. ..	Greenish amber.	Greenish amber.	Amber.
"    " <i>ex</i> gasoline ..	Amber.	Amber.	Amber.
"    " <i>ex</i> light oil ..	Amber.	Light amber.	Amber.
"    " <i>ex</i> crude oil ..	Amber.	Light amber.	Amber.

Remarks : The colour developed with the shale tar bases increased in intensity with increasing boiling point. The colours observed ranged through all the various shades mentioned but did not show quite as much difference as may appear to be indicated by the table.

filtered off and washed with 2-3 ml. of chloroform, the washings being collected separately. A positive test was indicated by the formation of a green colour in the chloroform washings.

(e) *Nickel Thiocyanate*. These tests were carried out as with the cupric salt using a 5% solution of nickel nitrate. With the solution of tar bases in gasoline a positive test was indicated by the formation of a green colour in the reagent and a white to green interfacial precipitate. Since the nickel thiocyanate was soluble in water the filtration step was not necessary. No precipitate was formed with the acid solutions of tar bases, but a positive test was indicated by the formation of an amber colour in the lower phase on shaking with chloroform.

(f) *Cobalt Thiocyanate*. These tests were carried out as with the cupric and nickel salts using a 5% solution of cobalt nitrate. As with the nickel salt, the cobalt thiocyanate did not precipitate and interfere with the observations of the test. With the tar bases in gasoline a positive result was indicated by the formation of a green precipitate. With the acid solutions a positive test was indicated by the formation of a greenish blue colour in the chloroform layer.

(g-i) *Cyanates (Carbamates)*. The formation of the dipyridine complex of cupric cyanate has been described for the detection of copper or cyanate, the complex being soluble in chloroform to give an azure blue solution (Morton, 1946 ; Werner, 1925 ; Vogel, 1945). The complex cobalt and nickel pyridine cyanates are also soluble in chloroform (Morton, 1946 ; Davis and Logan, 1928, 1934). Since potassium cyanate is not readily available commercially, it was prepared by two different methods for comparison ; the oxidation of fused potassium cyanide with litharge, and oxidation in solution with the calculated amount of potassium permanganate. In each case the freshly prepared solution gave the same results, and in each case also the solution decomposed on standing, so that no cyanate could be detected in the reagent solution after standing for a few hours even though the test applied was sensitive to one part of cyanate in 20,000 (Vogel, 1945), although this solution still gave

colour reactions with the tar bases, of comparable sensitivity with the acetates and thiocyanates. Hydrolysis of the cyanate would give a carbamate and then a carbonate, but carbonates did not give the colour reactions. It is therefore suggested that the colour reactions observed are due to the formation of complex pyridine cupric carbamate and the corresponding cobalt and nickel salts.

The cyanate (or carbamate) reagent was prepared by adding a solution of 5.5 gm. (0.033 gm. mol) of potassium permanganate in 40 ml. of water containing 3.3 ml. (0.033 mol) of concentrated hydrochloric acid to a solution of 3.3 gm. (0.05 mol) of potassium cyanide, followed by suction filtration to remove the precipitated manganese dioxide. The object of adding the acid was to neutralize the potassium hydroxide formed during the oxidation, but it did not appear to stabilize the cyanate solution and could be omitted without effect. The test was applied to the acid solutions of the bases only, as significant results could not be obtained with the gasoline solution of the bases. The test was carried out by adding two drops of the cyanate solution and two drops of the metal nitrate solution (as for the thiocyanate tests) to 5 ml. of the sample. Dilute (5%) acetic acid was added dropwise until the precipitated (hydroxide and/or carbonate of the metal) dissolved and the complex then extracted by shaking with 2 ml. of chloroform. A positive result was indicated by the formation of a colour in the chloroform layer. With a cyanate solution that had been freshly prepared the colours obtained were: copper, light blue; cobalt, royal blue; nickel, pale green. If the cyanate solution had been prepared for more than half an hour the colours obtained were: copper, green to amber, depending on the boiling range of the bases; cobalt, amber to red; nickel, orange to brown. Because of the instability of the fresh reagent the sensitivity of the test with only the more stable hydrolysed solution was determined.

#### (7) *Miscellaneous tests.*

In this section are listed those tests that cannot be included in any of the previous categories. The results are presented in Table 3.

(a) *Sodium Hydroxide.* Addition of this reagent to an acid solution of the bases liberates the free bases. Although pyridine itself is completely miscible with water, the solubility of the homologues decreases rapidly with increasing molecular weight. The test therefore depends on the sparing solubility of the liberated mixture of the bases in water. The reagent was used as a 10% aqueous solution and a positive result was indicated by the formation of a white precipitate or white cloudiness.

(b) *Condensation with Sodium 1:2-naphthaquinone-4-sulphonate.* Feigl and Frehden (1934) observed that *N*-alkyl pyridinium compounds readily condense with 1:2-naphthaquinone-4-sulphonic acid to give coloured compounds. The test was carried out using methyl iodide and dimethyl sulphate as alternative alkylating agents and gave yellow to red colours with the bases. However, similar colours were obtained in the absence of the bases when the test was applied to the gasoline and sulphuric acid used to dissolve the bases. This may be due to the condensation of the sulphuric acid reagent with other reactive compounds (Erlich and Herter, 1904).

(c) *Nessler's Reagent.* This reagent is the most sensitive reagent known for the detection of ammonia and has recently been shown to be even more sensitive for the detection of aromatic secondary amines than for ammonia (Liebhafsky and Bronk, 1948). Nichols and Willits (1934) thoroughly investigated the reaction of the reagent with ammonia and concluded that the product was a colloidal suspension of the composition  $\text{NH}_2\text{Hg}_2\text{I}_3$ . Primary and secondary amines could therefore be expected to give the analogous products  $\text{RNH}_2\text{Hg}_2\text{I}_3$ .

and  $\text{NR}_2\text{Hg}_2\text{I}_3$  respectively, and the tertiary amines may be expected to react as with Mayer's reagent. This reagent was prepared in the manner described by Perkin (1935). When tested with the heptane-octane mixture the reagent gave a slight yellow-green precipitate on standing for 10-15 seconds, in the absence of added tar bases. Because of this the sensitivity of the reagent for the detection of tar bases in gasoline solution was determined with solutions of the bases in a sample of the gasoline that had been washed with the reagent until no further precipitate was formed, and then water washed and filtered. The formation of a precipitate in the absence of added tar bases was probably due to the presence of aldehydes in the gasoline as it has been shown that Nessler's reagent can give a positive response to 1 p.p.m. of acetaldehyde in ether (van Deripe, Billheimer and Nitardy, 1936). With the solution of the bases in gasoline a positive test was indicated by the formation of a precipitate, the colour of which was usually greenish-yellow but, when near the limiting concentrations, was yellow to cream. With the acid solutions of the bases the reagent gave a white to cream precipitate.

#### SUMMARY.

Fifty-four different tests have been examined for their sensitivity for the detection of shale tar bases (essentially pyridine homologues). Thirty-nine of the tests are suitable for the detection of the lower boiling bases in solution in gasoline; 26 for the detection of the bases from the gasoline in solution in dilute acid; 33 for the detection of the bases from the light oil in solution in dilute acid; and 36 for the detection of the bases from the crude oil in solution in dilute acid.

#### ACKNOWLEDGEMENTS.

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## NITROGEN IN OIL SHALE AND SHALE OIL.

### IX. DENSITY-TEMPERATURE RELATIONSHIPS OF SHALE TAR BASES.

By GEO. E. MAPSTONE, M.Sc., A.A.C.I., A.R.I.C., M.Inst.Pet.

*Manuscript received, March 7, 1949. Read, April 6, 1949.*

#### INTRODUCTION.

In working with the tar bases isolated from the gasoline obtained by the thermal cracking of crude shale oil, it was frequently found necessary to apply temperature corrections to density measurements. Since the standard correction tables for petroleum products were not applicable to the bases and no coefficient of expansion data were available, the work reported here was carried out to make up the deficiency.

#### BASES USED.

A quantity of tar bases were liberated by caustic soda from the hydrolysed acid sludge from the refining of the gasoline as described previously (Mapstone, 1947). Four and a half litres of the bases were distilled from a one-gallon iron pot through a twelve pear glass fractionating column. The distillate was collected in seventeen 250 ml. portions which were used for the subsequent work.

A quantity of the light recycle oil from the Dubbs cracking plant was extracted with hydrochloric acid. The bases were recovered as above and, after drying over solid caustic soda, were distilled. The distillate was used for the subsequent work.

#### DENSITY DETERMINATIONS.

The density of the bases was determined to four significant figures with a Westphal balance. The vessel containing the sample was well lagged so that the density of the bases could be determined over a range of temperatures. The bases were heated to 80–90° C. and poured into the sample vessel. When the rate of cooling had become steady the density was determined. By taking reasonable precautions it was possible to obtain results reproduceable within the accuracy of the test (I.P. 59/45, 1948). Several other density determinations were carried out during the 1–2 hours required for the sample to cool to about 35° C. The sample was then chilled to about 5° C. and further density determinations were carried out on it as it warmed up. A minimum of six densities were determined on each sample at different temperatures.

The density-temperature relationships were determined for only ten of the eighteen samples as the specific gravities of the remaining samples were sufficiently close to others not to warrant their being checked.

When the observed densities were plotted against the temperature, a series of straight lines was obtained (Figure 1). Two fractions of the bases (Nos. 2 and 11) had the same density within experimental error, though there was a difference of 32° C. in their mean boiling points. This also indicated that the coefficient of expansion was a simple function of the density and not of the boiling point of the sample.

## COEFFICIENT OF EXPANSION.

The coefficient of expansion of each of the samples of the bases was calculated from the slope of the density-temperature curves from Figure 1. It was immediately evident that the coefficient of expansion was much higher than the corresponding figure for petroleum products and that it varied appreciably with the density of the bases. The coefficient of expansion did not give a perfect correlation when plotted against the density of the sample at 20° C. (read from Figure 1) but the results (Figure 2) indicated that the relationship was most probably linear. The method of Hanson (1947) was applied to determine the most probable correlation. This was

$$\alpha = 0.02739 - 0.01964 D_{20}$$

where  $\alpha$  = coefficient of expansion

$D_{20}$  = density of bases at 20° C.

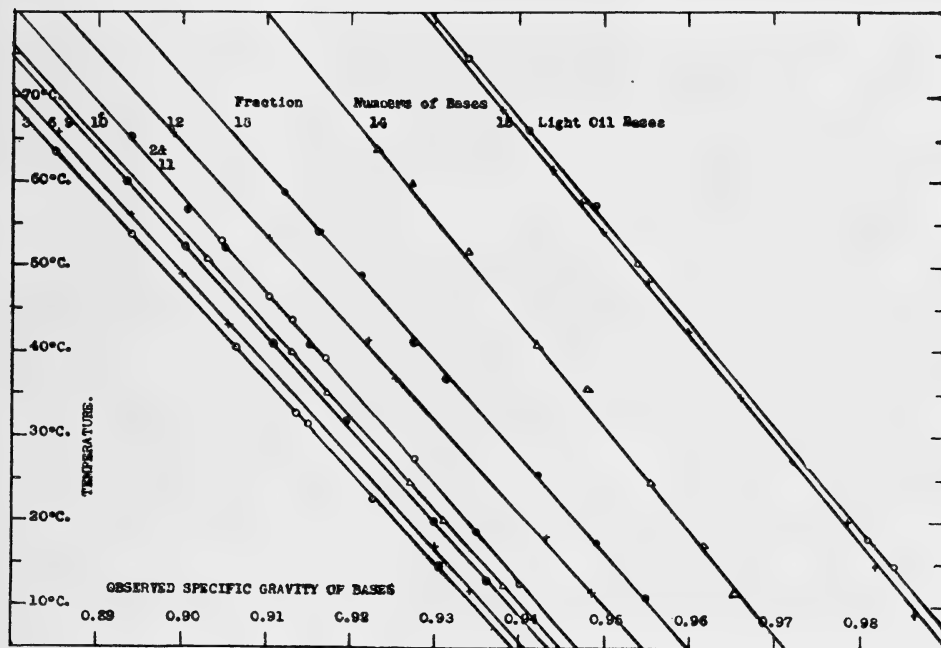


Fig. 1.—Variation of Specific Gravity of Tar Bases with Temperature.

Substituting this value of  $\alpha$  in the usual density correction formula

$$D_t = D_{20} - \alpha(t - 20) \dots\dots\dots (2)$$

where  $D_t$  = density at  $t^\circ$  C.

gives

$$D_t = D_{20} - (0.02739 - 0.01964 D_{20})(t - 20) \dots\dots (3)$$

as the overall relationship between the density and temperature for the shale tar bases. This relationship is presented in simple nomographic form in Figure 3. By means of this nomograph the density of any sample of the bases may be rapidly and simply corrected to 20° C. and, if required, calculated to any other temperature. The use of the nomograph is much simpler and more accurate than interpolation on Figure 1.

## BOILING POINT-DENSITY RELATIONSHIPS.

Since the tar base fractions used to determine the density-temperature relationships were mixtures, they distilled over fairly wide temperature ranges.

For purposes of comparison, therefore, the volumetric average boiling point was calculated for each sample as the average of the temperatures at which 10%, 30%, 50%, 70% and 90% of the material had distilled under standard conditions (I.P. 28/42). The results are expressed graphically in Figure 4, which shows that, with increasing volumetric average boiling point of the bases the density first decreased and then increased.

Relatively few data are available for the density of different fractions of shale tar bases, and those that are generally apply to carefully treated fractions and cannot, therefore, be expected to be representative of the crude bases. However, Cane (1942) reported the densities of some narrow boiling fractions from shale tar bases which had not been otherwise treated and these show an increase in density with the boiling point.

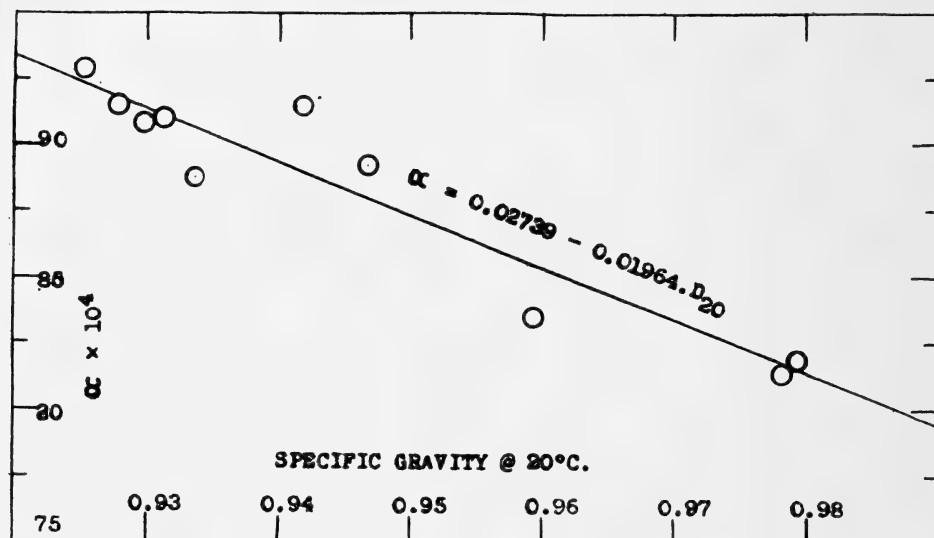


Fig. 2.—Correlation between Coefficient of Expansion and Specific Gravity of Shale Tar Bases.

The densities of alkyl pyridines, which appear to constitute the bulk of the bases, give a scatter relationship, as is to be expected, when they were plotted against the boiling points (Figure 4). By way of comparison with the unpurified bases, the data for pyridine homologues isolated from Fushun shale oil by Eguchi (1927, 1928) have been included in Figure 4. The densities recorded by Eguchi were corrected to 20° C. by means of Figure 3.

It is interesting to note that the density values for the crude tar bases lies within the spread of results for the purified bases isolated by Eguchi with the exception of the higher boiling fractions. However, the presence of a fair proportion of Eguchi's pyrindane or its homologues could readily explain the rapid increase in density with boiling point.

#### SUMMARY.

The variation of the specific gravity of shale tar bases with temperature has been determined and the coefficient of expansion has been correlated with the specific gravity at 20° C. The results are presented in the form of a nomograph. The specific gravity of the bases first decreases and then increases with the boiling point.

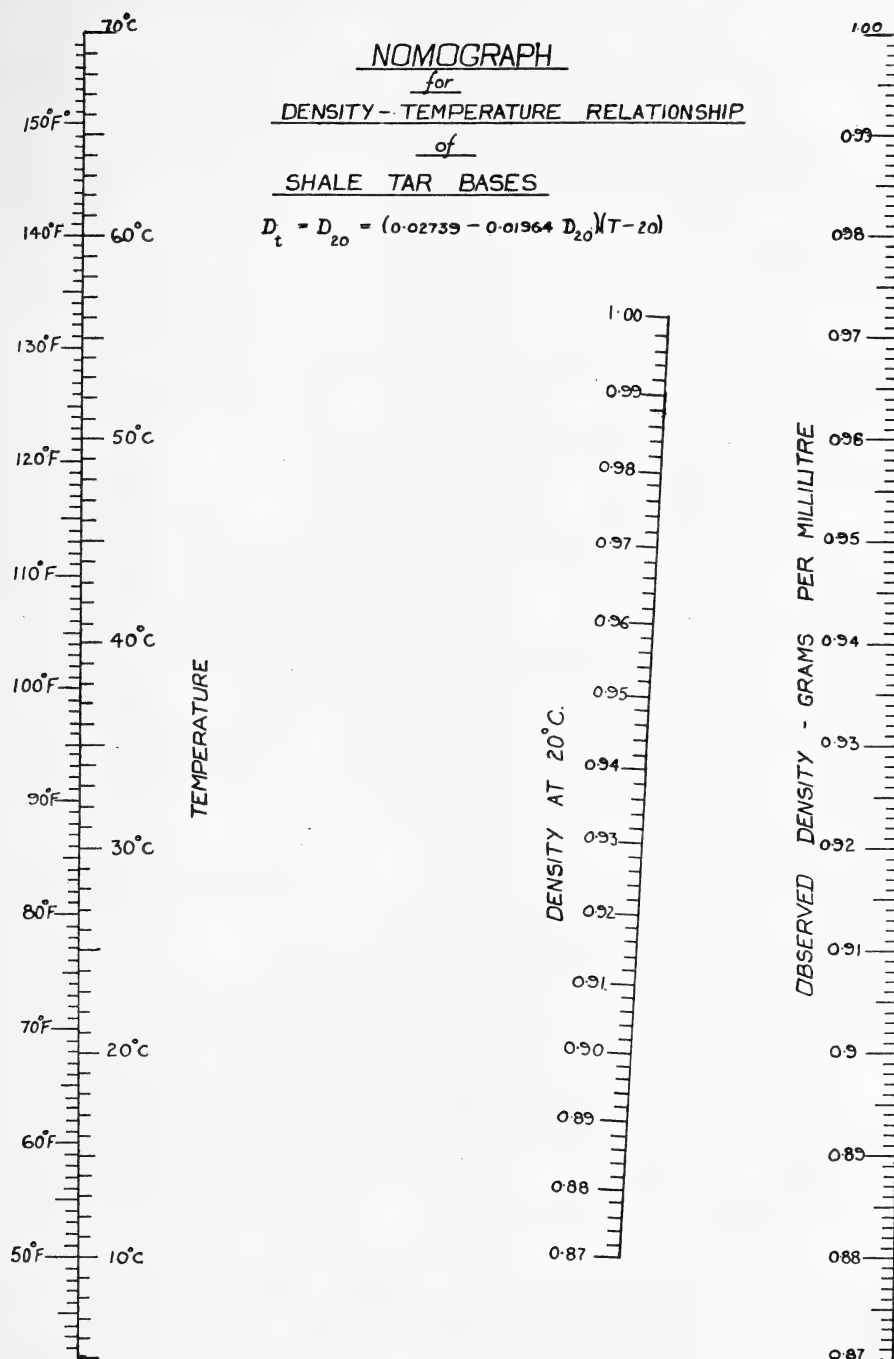


Fig. 3.

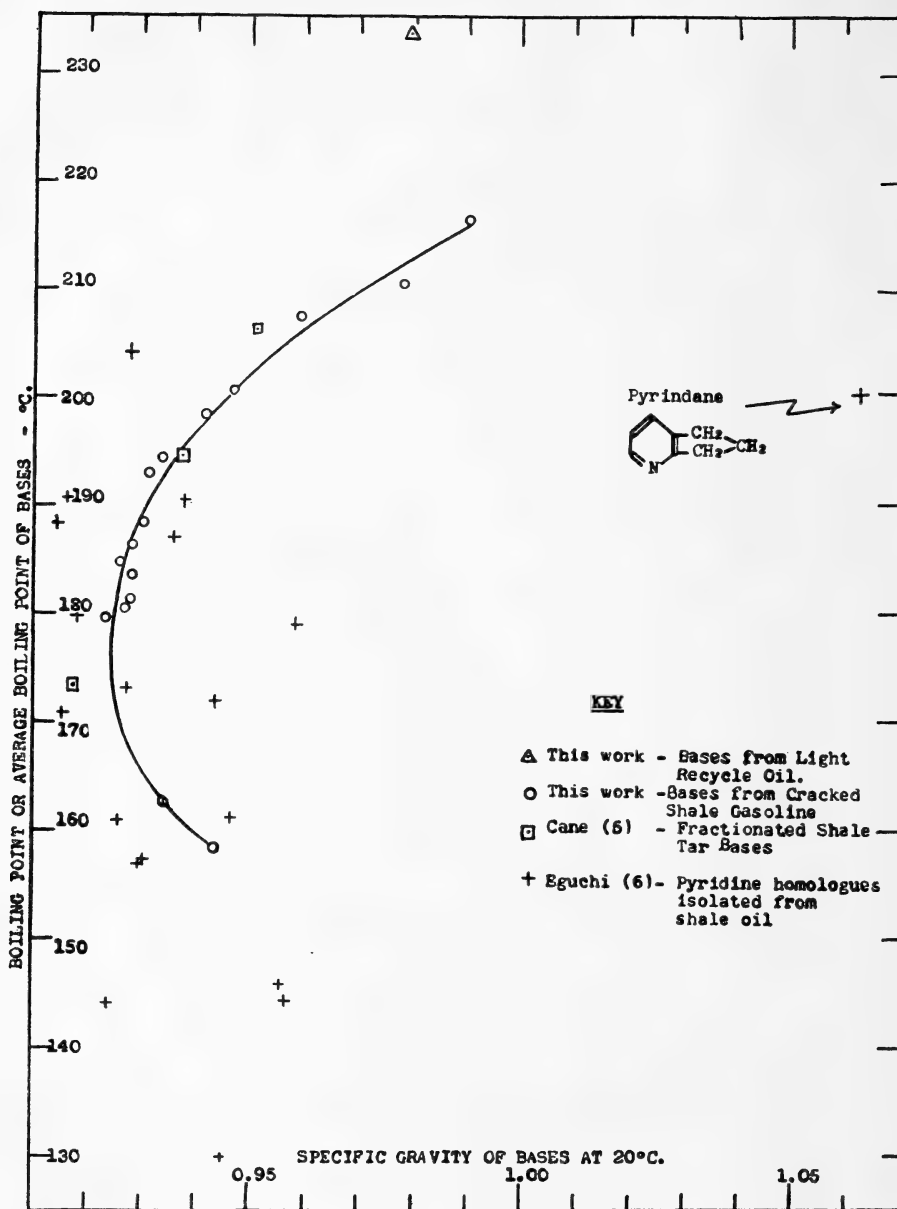


Fig. 4.

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# OCCULTATIONS OBSERVED AT SYDNEY OBSERVATORY DURING 1948.

By W. H. ROBERTSON, B.Sc.

(Communicated by the GOVERNMENT ASTRONOMER.)

*Manuscript received, December 16, 1948. Read, April 6, 1949.*

The following observations of occultations were made at Sydney Observatory with the 11½-inch telescope. A tapping key was used to record the times on a chronograph. No correction was applied to the recorded times, either for personal effect, or to allow for error in the Moon's tabular longitude. The reduction elements were computed by the methods given in the Occultation Supplement to the *Nautical Almanac* for 1938 and the reduction completed by the method given there. The necessary data were taken from the *Nautical Almanac* for 1948, the Moon's right ascension and declination (hourly table) and parallax (semi-diurnal table) being interpolated therefrom.

TABLE 1.

Serial No.	N.Z.C. No.	Mag.	Date.	U.T.	Observer.
				h m s	
164	429	6.9	Mar. 15	8 47 41.0	R
165	996	6.8	Apr. 15	8 13 24.1	W
166	1424	6.8	Apr. 18	10 25 56.3	W
167	1621	7.5	May 17	7 34 40.5	R
168	1864	6.8	May 19	12 18 28.3	R
169	1869	6.1	May 19	13 46 32.9	W
170	1598	6.4	June 13	9 51 11.9	W
171	2025	6.8	July 14	9 22 31.8	R
172	2228	5.9	Aug. 12	9 32 02.8	W
173	2398	6.1	Aug. 13	14 44 55.2	W
174	1946	7.2	Sept. 6	9 34 58.3	R
175	—	7.7	Sept. 6	9 41 06.1	R
176	2069	7.3	Sept. 7	10 21 41.7	W
177	2189	7.0	Sept. 8	9 13 10.4	R
178	2479	5.3	Sept. 10	11 25 02.6	R
179	2480	5.3	Sept. 10	11 25 15.8	R
180	2482	6.7	Sept. 10	11 46 10.4	R
181	2634	7.4	Sept. 11	12 21 55.4	W
182	2650	4.7	Sept. 11	14 36 51.7	W
183	2796	6.8	Sept. 12	12 11 46.0	W
184	3175	4.8	Sept. 15	11 08 35.0	W
185	3265	6.6	Oct. 13	10 42 10.0	R
186	3106	5.4	Nov. 8	13 40 17.2	R

Table 1 gives the observational material. The serial numbers follow on from those of the previous report (Robertson, 1948). The observers were H. W. Wood (W) and W. H. Robertson (R). In all cases the phase observed was disappearance at the dark limb. Table 2 gives the results of the reductions



TABLE 2.

Serial No.	Luna- tion.	$p$	$q$	$p^2$	$pq$	$q^2$	$\Delta\sigma$	$p\Delta\sigma$	$q\Delta\sigma$	Coefficient of	
										$\Delta\alpha$	$\Delta\delta$
164	312	+ 90	+43	81	+39	19	-1.6	-1.4	-0.7	+ 9.7	+0.73
165	313	+ 99	-12	99	-12	1	-0.3	-0.3	0.0	+13.1	-0.11
166	313	+ 99	-15	98	-15	2	-0.2	-0.2	0.0	+12.4	-0.47
167	314	+ 80	+60	64	+48	36	-2.3	-1.8	-1.4	+14.3	+0.21
168	314	+ 89	+46	79	+41	21	-1.5	-1.3	-0.7	+15.0	0.00
169	314	+ 98	+18	97	+18	3	-1.5	-1.5	-0.3	+14.4	-0.29
170	315	+ 87	-50	75	-43	25	-0.7	-0.6	+0.4	+ 8.5	-0.82
171	316	+ 92	+40	84	+37	16	-1.7	-1.6	-0.7	+14.7	-0.02
172	317	+ 94	-34	88	-32	12	-0.1	-0.1	0.0	+11.0	-0.62
173	317	+ 27	+96	7	+26	93	-1.0	-0.3	-1.0	+ 6.3	+0.89
174	318	+100	+ 4	100	+ 4	0	-0.6	-0.6	0.0	+13.5	-0.41
175	318	+ 99	+17	97	+17	3	-1.3	-1.3	-0.2	+14.1	-0.29
176	318	+ 84	-55	70	-46	30	+1.4	+1.2	-0.8	+ 8.0	-0.84
177	318	+ 81	+58	66	+47	34	-1.7	-1.4	-1.0	+13.6	+0.27
178	318	+ 74	-68	54	-50	46	+0.2	+0.1	-0.1	+ 8.5	-0.77
179	318	+ 73	-68	53	-50	47	+0.6	+0.4	-0.4	+ 8.4	-0.78
180	318	+ 90	-44	81	-40	19	0.0	0.0	0.0	+11.1	-0.56
181	318	+ 98	-19	96	-19	4	-1.0	-1.0	+0.2	+13.0	-0.22
182	318	+ 34	+94	12	+22	88	-1.4	-0.5	-1.3	+ 4.7	+0.93
183	318	+ 99	-15	98	-15	2	-1.0	-1.0	+0.2	+13.3	-0.06
184	318	+ 99	-16	97	-16	3	-0.1	-0.1	0.0	+13.9	+0.19
185	319	+ 98	-20	96	-20	4	-1.7	-1.7	+0.3	+14.1	+0.19
186	320	+100	+ 8	99	+ 8	1	-1.0	-1.0	-0.1	+12.9	+0.39

which were carried out in duplicate. The N.Z.C. numbers given are those of the Catalog of 3539 Zodiacal Stars for the Equinox 1950.0 (Robertson, 1940), as recorded in the *Nautical Almanac*.

The star involved in occultation 175 was not included in the *Nautical Almanac* list; it is G.C. 18326 (apparent place R.A. 13<sup>h</sup> 30<sup>m</sup> 44<sup>s</sup>.10, Dec. -8° 10' 14".0).

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# PROCESSES IN DIELECTRICS CONTAINING FREE CHARGES.

## THE ENTROPY OF ELECTROSTATIC SYSTEMS.

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### I. INTRODUCTION.

The dielectric behaviour of a space can be described in terms of its permittivity and conductivity, which then can be combined in a complex dielectric "constant"  $\epsilon$ . The permittivity, given by the real part of  $\epsilon$ , is a measure of the free electrostatic energy, which is available for doing reversible work, and is stored in the dielectric. The conductivity, which can also be expressed in terms of the dielectric loss angle  $\tan \delta$ , to which it gives rise, is a measure of the degree of how far the energetic state of the dielectric under applied electric stress is a state of labile equilibrium, i.e. how much energy must be expended in order to maintain that equilibrium state.

In an ideal vacuum condenser, all the energy stored in the field can be recovered without loss: it is free electrostatic energy, capable of doing reversible work. If the dielectric is filled with a polarizable substance, but still imagined loss-free, the energy stored will be greater depending on the permittivity of the substance, but it will still remain free electrostatic energy which can be reversibly recovered without loss.

Dielectric losses can arise from two fundamentally different causes: firstly, due to imperfections and losses in the polarization process, i.e. by the necessity for the expenditure of energy for the alignment and dealignment of the atoms and/or molecules, and secondly, due to the presence of free charges in the dielectric. A very considerable amount of study has been devoted to polarization losses. It is the purport of the present paper to investigate theoretically the influence of a space-charge in a dielectric on its dielectric behaviour.

### II. ANALYSIS.

An ideal vacuum condenser, of capacity  $C_{vac}$ , one plate of which is charged to a potential  $V$  with reference to the other plate, has stored free electrostatic energy  $W_f$  (capable of doing reversible work), and is given by

$$W_f = \frac{1}{2} V^2 C_{vac} \quad (1)$$

The sign of  $W_f$  depends on the point of view: following usual thermodynamic convention, it will be taken as negative if work equal to  $W_f$  can be done reversibly by the system.

If now the vacuum is filled with any material medium,  $V$  being maintained at its previous value, the quantity of free energy stored will be altered. It is therefore possible to define the electrostatic capacity of a system from equation (1):

$$C = 2W_f/V^2 \quad (2)$$

The permittivity of the dielectric, or the real part of  $\epsilon$ , will then be given by

$$\epsilon' = C/C_{vac} = D \quad (3)$$

Considering now a plane parallel condenser of unit area, whose plates are separated by a distance  $a$  and connected by resistance-less leads to a source of  $EMF = V$ : when the dielectric between the plates is a loss-free medium of permittivity  $D$ , the work done in charging the plates is  $W_0$ . Because the dielectric is loss-free, all the energy  $W_0$  then is free energy stored in the dielectric.

If now a space distribution of charges of local density  $\rho = f(x)$ , where  $x$  refers to a variable point in the dielectric  $x$  cm. distant from one plate, is introduced into the dielectric (the potential difference across the condenser being maintained at the previous value  $V$ ), additional work  $W_e$  will be necessary in order to do so.  $W_e$  will be stored in the condenser above and additional to the work  $W_0$  done in charging the loss-free condenser. The total energy stored in the condenser,  $W_t$ , is thus given by

$$W_t = W_0 + W_e \dots\dots\dots (4)$$

However, not all the energy  $W_t$  stored in the condenser which now contains free charges in its dielectric, will be free energy, since a quantity of energy  $W_\phi$  will be bound in the space charge itself. The total energy  $W_t$ , therefore, can be written as the sum of the free electrostatic energy  $W_f$  which is available for reversible work, and the unavailable energy bound within the space charge itself,  $W_\phi$ :

$$W_t = W_f + W_\phi \dots\dots\dots (5)$$

It should be stressed again that the potential difference across the condenser is maintained at a constant value  $V$  throughout the above operations. Combining equations (4) and (5) yields for  $W_f$

$$W_f = W_0 + W_e - W_\phi \dots\dots\dots (6)$$

The work  $W_e$  is done against  $V$ :

$$W_e = -VD(E'_a - E_0)/4\pi \dots\dots\dots (7)$$

where  $E'_a$  is the total field existing in the presence of the space-charges at the plate which is maintained at the potential  $V$  against the other plate.  $E_0$  is the Laplacian field in the absence of a space charge, given by

$$E_0 = -V/a \dots\dots\dots (8)$$

If a field  $E'$  is produced at a point  $x$  by the space charges, the energy bound within a space configuration of charges can be written

$$W_\phi = \frac{D}{8\pi} \int_0^a (E')^2 dx \dots\dots\dots (9)$$

Furthermore

$$dE'/dx = 4\pi\rho/D \dots\dots\dots (10a)$$

$$\int_0^a \rho dx = Q, \text{ the total charge/cm.}^2 \dots\dots\dots (10b)$$

The energy equation for the condenser containing free charges in its dielectric thus follows as

$$W_f = - \left[ C_0 V^2/2 + VQ + \frac{D}{8\pi} \int_0^a (E')^2 dx \right] \dots\dots\dots (11)$$

where  $C_0$  stands for the geometric capacity of the condenser in the absence of space charges, given by

$$C_0 = D/4\pi a = 2W_0/V^2 \dots\dots\dots (12)$$

In any actual case the term  $VQ$  in equation (11) will always be negative, since either  $V$  or  $Q$  will have to be negative, in order to maintain the space charge. The negative sign of  $W_f$  in equation (11) indicates that work equal to  $W_f$  can be done reversibly by the system.

From equation (11) the capacity and the permittivity of the charge filled dielectric follow by virtue of equations (2) and (3), once the field distribution within the dielectric is known. It is seen that the presence of a space charge leads to a diminution of the effective dielectric constant of the medium, a well known experimental fact which has been proved, e.g. for ionized gases, by Imam and Khashtgir (1937). In the appendix,  $C$  and the effective dielectric constant  $D$  are calculated for a simple but representative case, viz. a plane parallel diode obeying the Child-Langmuir  $3/2$  power law.  $D$  results as  $3/5$ , a value which has been obtained, *inter alia*, by Llewellyn (1941) from dynamical considerations. Another interesting case in point is the electric double layer confronting a polarized electrode in an aqueous solution.  $C_0$  is negligibly small in this case, since the whole condenser comes into being only by virtue of the ionic space charge. This problem will be dealt with in a separate communication.

As  $W_f$  represents free energy capable of doing reversible work, the laws of thermodynamics are applicable, if a one-to-one correspondence can be established between a given electrical and a thermal system having the same free energy  $G$ , so that  $G = W_f$ . The Gibbs Free Energy  $G$  is given by

$$G = U + W - TS \dots\dots\dots (13)$$

where  $U$  is the internal energy of the system,  $W$  the work done on the system,  $T$  the absolute temperature and  $S$  the entropy.

A thermal system where  $G = W_f$  can be constructed as follows:

Given a canonical distribution of elementary condensers each charged to a certain potential  $\psi$  and having an average density of charge  $\bar{\rho} = \text{Const.}$ , so that the total charge  $Q$  is also constant: following the standard statistical treatment (Lindsay, 1941) the entropy of the system is defined in terms of the distribution modulus  $\theta$ , which has the dimension of energy and can be interpreted as the average energy of every unit cell making up the statistical ensemble. In the case of a thermal system, these unit cells are particles (say gas molecules) with an average energy of  $kT/2$ , measured in thermal units. In the case of an electrical system, the average energy equals  $\bar{\rho}\psi/2$ , measured in electrical units, and each cell represents one elementary condenser. Integrating over the whole system, its energy becomes equal to  $QV/2$ , where  $V$  is the potential appearing across the plates of the resulting macroscopic condenser, while the energy of the thermal system becomes equal to  $RT/2$ . As the energy of the electrical and that of the corresponding thermal system are equal, it follows that<sup>1</sup>

$$QV = RT = \theta \dots\dots\dots (14)$$

An ideal gas is characterized by

$$C_p - C_v = \text{Constant} = R \dots\dots\dots (15)$$

The gas law  $pv = RT$  then holds,  $C_p$  and  $C_v$  being the specific heat at constant pressure and constant volume, respectively, and  $p$  the pressure and  $v$  the volume. This is the equivalent to the restriction imposed on the electrical system by the condition that  $Q = \text{Constant}$ . If  $Q \neq \text{Constant}$ , the electric system corresponds to a non-ideal gas where equation (15) no longer holds, i.e. where  $R = f(T \dots)$ .

Equation (14) shows that appropriate values have to be assigned to  $V$  and  $T$ , because  $Q$  and  $R$  (for an ideal gas and its electric counterpart) are constants. Therefore, if  $V$  is given,  $T$  is uniquely determined, and *vice versa*. A one-to-one correspondence thus exists between these two quantities.

An analogue between  $V$  and  $T$  has first been proposed by Mach (1871, 1919) and Lippmann (1876). The electric-current thermal-current analogue is well known (Avrami and Paschkis, 1942) and recently Bosworth (1946) has established the thermal equivalent of the Ohm, Farad and Henry.

<sup>1</sup> Equation (14) in the form  $V^2C/2 = kT/2$  has been first used by Einstein (1907) in a treatment of the effect of Brownian motion on the potential across a condenser.

The one-to-one correspondence between  $V$  and  $T$  having been established, it also follows from equation (14) that  $Q = \int_0^a \rho dx$  corresponds to  $R$ . The product  $RT = pv$  thus corresponds in the electrical case to  $W_e$ .

As to the enthalpy  $H$ , the counterpart of the total energy  $W_t$  of the electrical system, it can be written

$$H = U + W \dots\dots\dots (16)$$

Since it has been shown that  $W = pv = RT$  corresponds to  $W_e = QV$ ,  $U$  is seen to be in one-to-one correspondence with  $W_o$ , since the electric and the corresponding thermal system are to have equal energy.  $W_o$  electrically also behaves similarly to  $U$  in a cyclic process, because it returns to its initial value when  $V$  (or  $T$  in the thermal case) is first increased and then allowed to return to its former value. In other words, the internal energy in the thermal case is a single valued function of  $T$  exactly as the energy stored in the geometric capacitance of a condenser is a single valued function of the potential to which it is charged. It is now seen that the term  $TS$  in the thermal case, equation (13), corresponds to the term  $W_\phi$  in the electric system described in equation (6). Since  $T$  has been shown to be in one-to-one correspondence to  $V$ , the quantity  $W_\phi/V$ , which it is proposed to call the ELECTRICAL ENTROPY, similarly corresponds to the thermal entropy  $S$ . More accurately, the differential change in the electrical entropy  $dS_e$ , defined by

$$dS_e = \frac{dW_\phi}{V} \dots\dots\dots (17)$$

is in one-to-one correspondence to the entropy element

$$dS = \frac{dq}{T} \dots\dots\dots (18)$$

For a rigid proof that equation (17) represents an entropy element it must be shown (1) that  $dW_\phi$  is not an exact differential, and (2) that  $1/V$  is an integrating factor making  $dW_\phi/V$  exact.

Since  $W_\phi$  is a function of  $V$ ,  $\oint W_\phi dV$  would vanish if  $dW_\phi$  were exact. From equations (4) and (5)  $W_\phi$  can be written

$$W_\phi = W_t - W_f \dots\dots\dots (19)$$

If  $\oint W_\phi dV = 0$  would hold,  $\oint W_t dV$  would vanish also, since  $\oint W_f dV$  vanishes by definition of  $W_f$  as free energy available for reversible work. But in general  $\oint W_t dV \neq 0 \dots\dots\dots (20)$

since work might be done on or by the system. Therefore contention (1) is proved.

As to the second proposition, it must be shown that

$$\oint \frac{dW_\phi}{V} = 0 \dots\dots\dots (21)$$

Again, since  $\oint W_f dV = 0$ , equation (21) can be written, using equation (5), thus :

$$\oint \frac{W_e}{V} dV = 0 \dots\dots\dots (22)$$

Assume that this were not true. It then would be possible by repeating the cyclic process of first increasing and thereafter decreasing  $V$  to its initial value, to increase the total space charge  $Q$  without limit (always assuming the potential changes to be slow compared with the relaxation time of the process, or in other words slow enough to allow the charge distribution to come into equilibrium for all intermediate values of  $V$ ). This would be against experience and against the laws of thermodynamics. The proposition, therefore, is proved.

The electrical entropy of an electrostatic system where  $Q = \text{constant}$  follows directly from the statistical considerations on page 68 and equation (14), as

$$(S_e)_{Q=\text{const}} = Q \log (V/N!) \dots\dots\dots (24)$$

where  $N$  is the number of unit cells comprising the statistical ensemble, and therefore an additive constant. Equation (24) is thus seen to be formally identical with the Boltzmann relation

$$S = k \log w + \text{const} \dots\dots\dots (25)$$

where  $w$  is a measure of the probability of the system to be found in a state determined by the energy of the statistical canonical distribution modulus  $\theta$ .

Furthermore, it is seen that the electrical entropy thus comes within the scope of definition of entropy as a measure of the extension of an equilibrium state, as given by Postma (1916). Equation (24) can also be derived from equation (17), which can be written

$$dS_e = \frac{1}{V} \frac{dW_\phi}{dV} dV \dots\dots\dots (26)$$

for  $Q = dW_\phi/dV = \text{Constant}$ .

Table 1 lists the two sets of quantities shown to be in one-to-one correspondence with each other:

TABLE 1.

Electrical Quantity.	Thermal Quantity.
Free electrostatic energy $W_f$ .	Gibbs' free energy $G$ .
Energy stored in condenser in the absence of space charges, $W_0$ .	Internal energy $U$ .
Work done in introducing the space charges, $W_e$ .	Work done by or against external forces, $W$ .
Potential $V$ .	Temperature $T$ .
Volume of the condenser $v$ .	Volume of the gas $v$ .
Energy bound in the space charge, $W_\phi$ .	$TS$ .
The product potential $V$ by average space charge density $\bar{\rho}$ .	Average pressure of the gas, $\bar{p}$ .
Total energy $W_t$ .	Enthalpy $H$ .
Total charge $Q = \int \rho dv$ .	Gas constant $R = C_p - C_v$ .
Electrical entropy $dW_\phi/V$ .	Entropy $dq/T$ .

All the electrical quantities are time-variable to the extent that  $V$  is a function of time. Moreover, if a cyclic process is considered by first increasing  $V$  to a predetermined value and then reducing it again to its initial value, then the time taken for such a cycle must be large compared with the relaxation time of the readjustment of the system to the altered field. This is the exact counterpart to the thermal case where in an isochoric cycle the change of  $T$  must not be too fast for the thermal conductivity of the gas. In both cases, the rate of change of  $T$  or  $V$ , respectively, must be sufficiently small to permit consideration of the whole gas or dielectric as in a state of thermal or electrical equilibrium for every intermediate value of  $T$  or  $V$ . Since the temperature  $T$  represents an absolute, irreducible, dimensional quantity which enters into the dimensions of thermal quantities, it is clearly impossible to bring all thermal and the corresponding electric units to the same dimensions. The electric quantities, in the electrostatic system, are based upon the permittivity of free space, which enters into their dimensional formulae and which equally represents an absolute and irreducible dimensional quantity. However, there are some cases where the corresponding electric and thermal quantities also have the same dimension, even if that cannot

be expected in general. The pressure  $\bar{p}$  and  $\bar{\rho}V$  present such an exceptional case, having the same dimension ( $ml^{-1}t^{-2}$ ).

The second law of thermodynamics can now be applied to a purely electrical system :

EVERY PURELY ELECTRICAL PROCESS WILL TAKE PLACE IN SUCH A MANNER THAT THE ELECTRICAL ENTROPY OF THE SYSTEM INCREASES.

This can take place either by the increase of the bound energy  $W_\phi$ , by the decrease of the potential difference  $V$ , or by a combination of both processes. Moreover, in correspondence to the thermal case,  $dS_e = V^{-1}dW_\phi$  is an exact differential and the electrical entropy completely and uniquely describes the electrical state of the system.

The following examples might serve to illustrate the application of this law :

- (i) A SOLID DIELECTRIC UNDER ELECTRIC STRESS HIGH ENOUGH TO PRODUCE IONIZATION :

Once ionization sets in, i.e. free charges appear, the dielectric constant of the medium decreases (Imam and Khastgir, 1937) ( $W_\phi$  increasing and  $W_t$  therefore decreasing). At the same time the conductivity of the dielectric increases (the potential  $V$  across it is lowered unless maintained from outside), as is well known.

- (ii) A REVERSIBLE ELECTRODE REACTION :

Increase of concentration of dischargeable ions (i.e. increase of free charges) reduces the discharge potential ( $V$  decreases). At the same time a higher potential is needed before the limiting current is reached because a greater proportion of the energy supplied,  $W_t$ , is transformed into unavailable energy  $W_\phi$ . Both effects are well known experimental facts (Kolthoff and Lingane, 1941).

The entropy of a perfect monatomic gas is given by

$$S = \frac{5}{2}R \log T - R \log \bar{p} + \text{Const.} \dots\dots\dots (27)$$

In the corresponding electrical system this becomes, by virtue of equivalences listed in Table 1,

$$S_e = \frac{5}{2}Q \log V - Q \log \bar{\rho}V + \text{Const.} \dots\dots\dots (28)$$

$$= \frac{3}{2}Q \log V - Q \log \bar{\rho} + \text{Const.} \dots\dots\dots (29)$$

The average charge density  $\bar{\rho}$  in the electrical counterpart of a perfect gas being constant (see page 68, equations (14) and (15) and following), equation (29) can be expressed thus :

$$S_e = \frac{3}{2}Q \log V + \text{another constant} \dots\dots\dots (30)$$

A monatomic gas having three degrees of freedom, the electrical entropy of the corresponding electrical system, *per degree of freedom*, results as

$$S_{e/t} = \frac{Q}{2} \log V + \text{Constant} \dots\dots\dots (31)$$

However, the space charge element in a plane parallel condenser has only two degrees of freedom of translatory motion, which also follows from Gibb's Phase Rule : If  $C$  is the minimum number of components required to describe each phase of the system completely and  $P$  is the number of phases, the degrees of freedom  $F$  are given by

$$F = C - P + 2 \dots\dots\dots (32)$$

Thus in the electric system  $P=2$ , corresponding to free energy and bound energy and  $C$  is equal to 2, corresponding to the charge and the potential, describing each phase.  $F$  therefore equals 2. The total electrical entropy of an electrical system where  $Q=\text{Constant}$ , therefore follows as

$$S_e = Q \log V + \text{Constant} \dots\dots\dots (33)$$

This equation thus has been derived from purely thermodynamical considerations by application of the one-to-one correspondences listed in Table 1. As can be seen, equation (33) is identical with equation (24), which was derived directly from the statistics of the electrical system. This, then, is an example for the correctness of applying thermodynamic reasoning to electrical processes.

If the potential  $V$  on one plate of the condenser is reduced to another value  $V'$ , a certain amount of energy  $W_\phi$  will not appear as available energy, but will be dissipated or irreversibly expended. In parallelism to a thermal process,  $W_\theta$  can be calculated from the electrical entropy  $S_e$ :

$$W_\phi = V' \int_{V'}^V \frac{1}{V} dW_\phi = V' \int_{V'}^V F\left(x, V, \frac{dV}{dx}\right) dx \dots\dots\dots (34)$$

It is of interest to find some conditions which make  $W_\theta$  vanish or a minimum  $\neq 0$ . It is obvious that if  $W_\theta=0$  or  $V'=0$ ,  $W_\theta$  also will vanish. The former case is trivial, since it amounts to a condenser without space charge. The latter can be realized only by connecting the condenser plates for a time sufficient to allow *complete* discharge. It is known, however, from the phenomenon of dielectric absorption that the rate of decay of  $W_\phi$  in general even after the removal of  $V$  is slow (Gross and Denard, 1945). To find the conditions which make  $W_\theta$  a minimum  $\neq 0$ , Euler's equation is set up for the path which makes the integral in equation (34) a minimum:

$$\frac{\partial^2 F}{\partial \rho \partial x} + \frac{\partial^2 F}{\partial V \partial \rho} \frac{dV}{dx} + \frac{\partial^2 F}{\partial \rho^2} \frac{d^2 V}{dx^2} = 0 \dots\dots\dots (35)$$

where  $F = F\left(x, V, \frac{dV}{dx}\right)$  and  $p = -dV/dx$ . In the present case,  $F = \frac{(E')^2}{V}$

and  $p = -dV/dx = (E' + E_0)$ . It is seen that  $F = \text{Const.}$  is one solution of equation (35). This is the special case of a dielectric where

$$(E')_a = \frac{4\pi Q}{D} = \text{Const. } V^{\frac{1}{2}} \dots\dots\dots (36)$$

The connection between this condition and the well-known Debye-Hueckel equation will be dealt with in a separate communication.

Another solution of equation (35) is  $p = \text{Constant}$ :

$$\begin{aligned} dV/dx &= \text{Constant} \\ V &= \text{Const.} \cdot x + \text{Constant} \dots\dots\dots (37) \end{aligned}$$

i.e. a linear relationship between local potential  $V$  and  $x$ , or, therefore, the condition that the *total* potential is Laplacian. The system thus will operate under minimum energy dissipation if the externally applied field  $E_0$  and the field due to the space charges cancel at the condenser plates, i.e. when the system is in potential equilibrium at the plates. This is possible only in a region of space charge where  $E_0 = -4\pi Q/D$ . This is equivalent to  $dQ/dV = \text{Const.}$ , which plays a similar role to the specific heat in thermal processes. For the reversibility of the electric process, therefore, it is sufficient if the *total* space charge present is either constant or linearly proportional to the potential across the condenser. This condition does not imply a purely static case, i.e. the absence



of a space-current: it suffices if  $\text{div } (\partial \rho / \partial t)$  is either constant or linearly proportional to  $V$ . In other words, a dielectric may contain free charges and still be loss-free, subject to the above conditions. Physically, these can be interpreted as meaning that for minimum electrical waste energy the field at the plate must be in equilibrium with the field of all space charges in the dielectric. Such systems actually exist in nature; they are approached in electro-chemical reactions, in the region in front of the plate (or in the space between plate and suppressor) of a pentode, where the plate current is nearly independent of the plate potential, and also by a triode biased to cut-off, so that the field due to the grid, plate and electrons exactly balance.

The capacity defined in equation (2) represents the  $d$ - $c$  capacity measurable after a steady state has been attained. For varying and for alternating potentials a capacity  $C_d$  is defined by the differential

$$C_d = dq_o / dV$$

$$q_o = 2W_t / V \dots\dots\dots (38)$$

$q_o$  being the free charge. Since the derivative  $dQ/dV$  enters into the expression for  $C_d$ , it is seen that the *change* in the free energy and with it  $C_d$ , depend on the relaxation time of  $Q$ . In other words, the ideally reversible free charge is truly so only for infinitely small (i.e. infinitely slow) changes of  $V$ , since it will always take a finite time for  $Q$  to adjust itself to a change in  $V$ . This time, as has been pointed out by Gross and Denard (1945), may be extremely long, in some cases even hundreds of thousands of years. It is another example of processes, so well known to thermodynamics and chemical kinetics, processes which are only partly reversible in practice, while in themselves they are inherently completely reversible reactions.

### III. SUMMARY.

The free electrostatic energy, capable of doing reversible work, stored in a space-charge filled condenser, is calculated, yielding an expression for the effective dielectric constant of a medium containing free charges.

A one-to-one correspondence between a number of thermal and electrical quantities is established. The electrical entropy  $S_e$  is defined as  $dS_e = V^{-1}dW_\phi$ ,  $V$  being the potential difference across the condenser and  $W_\phi$  the energy bound within the space configuration of charges. It is proved that  $dS_e$  is an exact differential. The second law of thermodynamics is applied to purely electrical systems in the form: Every purely electrical process will take place in such a manner that the electrical entropy of the system increases.

Further equivalences between electrical and thermal processes are demonstrated. It is shown that a space charge filled condenser may still be loss free, if the sum total of the free charges in its dielectric is constant or linearly proportional to the potential difference across the condenser.

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### V. APPENDIX.

The Child-Langmuir  $3/2$  power law for a plane parallel diode can be written thus (Koller, 1937):

$$V = \left[ \frac{Jx^{2/3}\pi}{(2e/m)^{1/2}} \right]^{2/3} \dots\dots\dots (39)$$

where  $J$  is the space current density,  $x$  a variable point where a local potential  $V$  exists (at the plate,  $x=a$ , the interelectrode spacing and  $V=V_0$  the plate voltage), and  $e/m$  the specific electronic charge. The space charge being *in vacuo*:

$$\frac{D}{8\pi} \int_0^a (E')^2 dx = \frac{1}{8\pi} \frac{16\pi(9\pi)^{1/3} J^4/3 a^{5/3}}{(2e/m)^{2/3}} \frac{3}{5} \dots\dots\dots (40)$$

Since

$$\rho = V/v = \frac{J V^{-1/2}}{(2e/m)^{1/2}} \dots\dots\dots (41)$$

where  $v$  is the average local velocity of the electrons, given by

$$mv^2/2 = eV \dots\dots\dots (42)$$

$Q$  results as

$$Q = \int_0^a \rho dx = \frac{J}{(2e/m)^{1/2}} \int_0^a V^{-1/2} dx \dots\dots\dots (43)$$

But from equation (39):

$$V^{-1/2} = \left[ \frac{Jx^{2/3} 9\pi}{(2e/m)^{1/2}} \right]^{-1/3} \dots\dots\dots (44)$$

Therefore

$$Q = \frac{J}{(2e/m)^{1/2}} \int_0^a \left[ \frac{9\pi J}{(2e/m)^{1/2}} \right]^{-1/3} x^{-2/3} dx \dots\dots\dots (45)$$

yielding on integration

$$Q = \frac{J^{2/3} 3a^{1/3}}{(9\pi)^{1/3} (2e/m)^{1/3}} \dots\dots\dots (46)$$

Recalling equations (2), (11) and (12) for  $C$ ,  $W_f$  and  $C_0$  respectively, it follows on substitution that

$$D = C/C_0 = -1 + \frac{8}{3} - \frac{16}{15} = \frac{3}{5} \dots\dots\dots (47)$$

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# THE EFFECT OF pH UPON THE ULTRA-VIOLET ABSORPTION SPECTRA OF PYRIDINE TYPE COMPOUNDS.

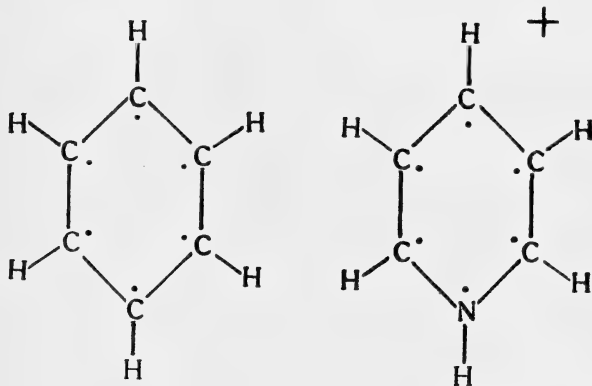
By L. E. LYONS, B.A., M.Sc.

*Manuscript received, March 30, 1949. Read, May 4, 1949.*

## INTRODUCTION.

Previous studies by Loofbourov and Stimson (1940) and Craig and Short (1945) have shown that the ultra-violet absorption of such N-containing substances as barbituric acid, guanine, adenine and the various aminoacridines changes with pH. An explanation for the former group has been given in terms of tautomers and for the second in terms of ions.

The present study was undertaken with a view to determining the molecular species present at different pH's, to assist in the interpretation of polarographic curves, but the results may be of interest to those concerned in the theoretical investigation of the energies of molecular  $\pi$ -orbitals, as the introduction of  $H^+$  into, say, pyridine adds no electrons and gives a resultant molecule which in some ways resembles benzene, having a similar distribution of nuclei :



The difference from benzene is twofold : (i) the symmetry of the molecule is lessened by the presence of N instead of a C ; and (ii) an excess positive charge is present. The effect of (i) would be expected as a blurring of the vibrational partial band structure and of (ii) as an alteration in the energies of the molecular orbitals, necessitating different values given to certain integrals in the theoretical treatment, and being revealed in a shift in the wave number of the corresponding band. Furthermore, it was thought possible that the results might throw some light on vibrational modes of the free base molecules.

## EXPERIMENTAL.

All measurements were made on a Beckmann ultra-violet spectrophotometer with a hydrogen discharge lamp as light source. Each substance used was dried and purified by either repeated fractionation or crystallization.

The strength of all solutions was  $10^{-4}$  M.

## RESULTS.

The results are graphed and tabulated, together with some values in hydrocarbon solvents obtained from the literature.

$\epsilon$  is defined by the relation  $I = I_0 10^{-\epsilon cd}$

where  $I$ ,  $I_0$  are transmitted and incident light intensities,

$c$  is molar concentration,

$d$  is cell thickness (cm.).

## DISCUSSION OF RESULTS.

1. The formation of the  $\equiv\text{NH}^+$  ion at pH 4 from the free base,  $\equiv\text{N}$ , is consistent with the results, as will be seen from the following; which means that the absorption at the lower pH is in every case by a molecular species different from that which absorbs at pH 7. A further change of pH from 7 to 10 should accordingly produce no further change in the nature of the absorption. This was tested, and the results were as expected except that with quinaldinic acid there was a slight difference in the absorption curves at pH 7 and 10. However, this is easily explicable in view of the presence of the carboxyl group and its possible ionization as well as a certain amount of zwitterion formation. Thus the results confirm the attribution of the spectral differences to the presence of different molecules and conversely enable the latter to be identified from the spectra.

2. The differences in spectra at pH's 4 and 7 are of two sorts: (a) a change in  $\nu_1$ , the wave-number of the first maximum, i.e. the maximum corresponding to the least possible energy difference in a transition between lower and upper states of the absorbing molecule, and in which a minimum of the absorbed energy is used to excite higher vibrational levels in the upper state; and (b) a change in the intensity of absorption measured by  $\epsilon$ , and in particular a change in  $\epsilon_1$ , the value at  $\nu_1$ .

TABLE 1.

Substance.	Solvent.	$\nu_1$ .	$\epsilon_1$ .	$\nu_2$ .	$\epsilon_2$ .	$\nu_3$ .	$\epsilon_3$ .
Pyridine(1) .. ..	pH 4.	39,150	5,200	> 40,500	—	—	—
„ .. ..	pH 7.	39,200	2,650	39,840	2,400	> 40,500	—
„ .. ..	Iso-octane(2).	39,100	1,660	39,600	1,760	—	—
Quinoline(1) .. ..	pH 4.	32,050	5,850	—	—	—	—
„ .. ..	pH 7.	32,050	2,950	33,300	3,100	35,700	3,280
„ .. ..	Hexane(3).	32,100	6,310	—	—	—	—
Iso-quinoline(1) .. ..	pH 4.	30,200	4,200	37,040	2,220	> 40,500	—
„ .. ..	pH 7.	31,450	2,560	32,570	2,220	37,750	3,080
„ .. ..	Hexane(3).	31,700	3,160	—	—	—	—
Quinaldine(1) .. ..	pH 4.	31,750	7,300	> 40,500	—	—	—
„ .. ..	pH 7.	33,170	3,600	36,100	3,500	—	—
Quinaldinic acid(1) .. ..	pH 4.	31,250	6,550	> 40,500	—	—	—
„ .. ..	pH 7.	34,400	4,250	> 40,500	—	—	—
2-picoline(1) .. ..	pH 4.	38,050	7,200	38,300	7,200	—	—
„ .. ..	pH 7.	38,250	4,860	—	—	—	—

(1) At pH 4 will be in the form of the ion.

(2) American Petroleum Institute Research Project 44, National Bureau of Standards Catalog of Ultraviolet Spectrograms, Serial No. 108.

(3) International Critical Tables, V (1929).

3. Changes in  $\nu_1$  did not occur in the cases of pyridine, 2-picoline and quinoline but did occur in every other case as a shift towards the red with change of pH from 7 to 4. The magnitude of the shift varied, although that in quinaldine was equal to that in iso-quinoline. It is unlikely that the quinaldine acid shift which is far greater than either of the latter two is comparable because of the obliteration of all the partial band structure in the quinaldine acid spectrum at pH 7 and consequent measurement of  $\nu_1$ , at a higher value than that corresponding to a transition to the lowest possible vibrational level of the upper state. The increasing blurring of structure is consistent with introduction of progressively more massive groups into the quinoline nucleus in the order  $-\text{H}$ ,  $-\text{CH}_3$ ,  $-\text{COOH}$ . No explanation can be advanced at present for the similarity of the shift in the cases of quinaldine and iso-quinoline.

The similarity of  $\nu_1$  for pyridine (2-picoline, quinoline) and its ion means that the introduction of a hydrogen nucleus and of a positive charge into the molecule has the same effect on the energy of each level concerned in the transition, thus preserving a constant difference between the two. It does not necessarily mean that the introduction of a positive charge is without any effect on the potential energy of the molecular orbitals; it would be remarkable if this were so, since it would imply that the field in which the electrons moved was unaffected by the increased nuclear charge.

4. Change in  $\epsilon_1$  was invariably an increase as the pH changed from 7 to 4. The values of  $R [=(\epsilon_1)_{\text{pH } 4} : (\epsilon_1)_{\text{pH } 7}]$  are given in Table 2.

TABLE 2.

Substance.					R
Pyridine	..	..	..	..	1.98
2-picoline	..	..	..	..	1.50
Quinoline	..	..	..	..	1.98
Iso-quinoline	..	..	..	..	1.63
Quinaldine	..	..	..	..	2.03
Quinaldine acid	..	..	..	..	(1.70)(1)
Acridine(2)	..	..	..	..	2.2
Mean	..	..	..	..	1.9

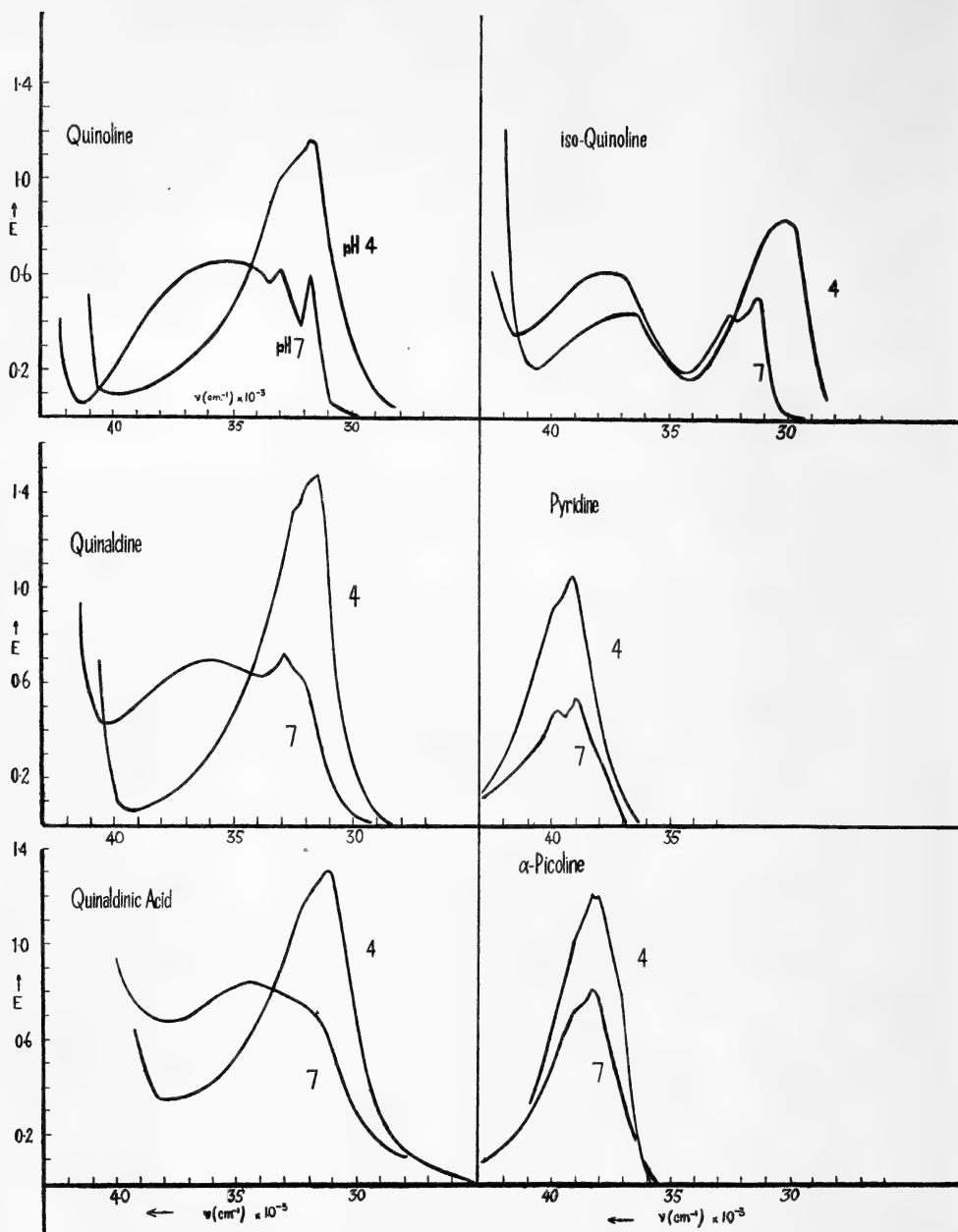
(1) This figure is not strictly comparable for the reason mentioned above and is omitted from the mean.

(2) Calculated from graphs of Craig and Short (1945).

Although a better method of measuring the intensity of absorption is by the area enclosed by the curve, the values obtained for  $R$  show clearly the general trend and the closeness of the values for pyridine, quinoline and quinaldine is especially interesting, as is the similarity of the absolute value of  $\epsilon_1$  for pyridine and quinoline, indicating that the fusion of a benzene ring with a pyridine ring is without effect upon the intensity of short wave-number absorption despite the shift in the location of the absorption.

5.  $\epsilon$  at other wave-numbers was in every case greater over a considerable range at pH 7 than at pH 4. However, the total absorption as measured by the

area  $\int_{\nu=0}^{40,000 \text{ cm.}^{-1}} \epsilon d\nu$  was always about 25% greater at pH 4 than at pH 7.



It is hoped to consider the spectra of these molecules from a theoretical point of view at a later date.

6. By noting the pH at which the absorption changes from that of  $\equiv\text{NH}^+$  to that of  $\equiv\text{N}$  a method is available for determining the pK value of  $\equiv\text{NH}^+$  compounds.

## SUMMARY.

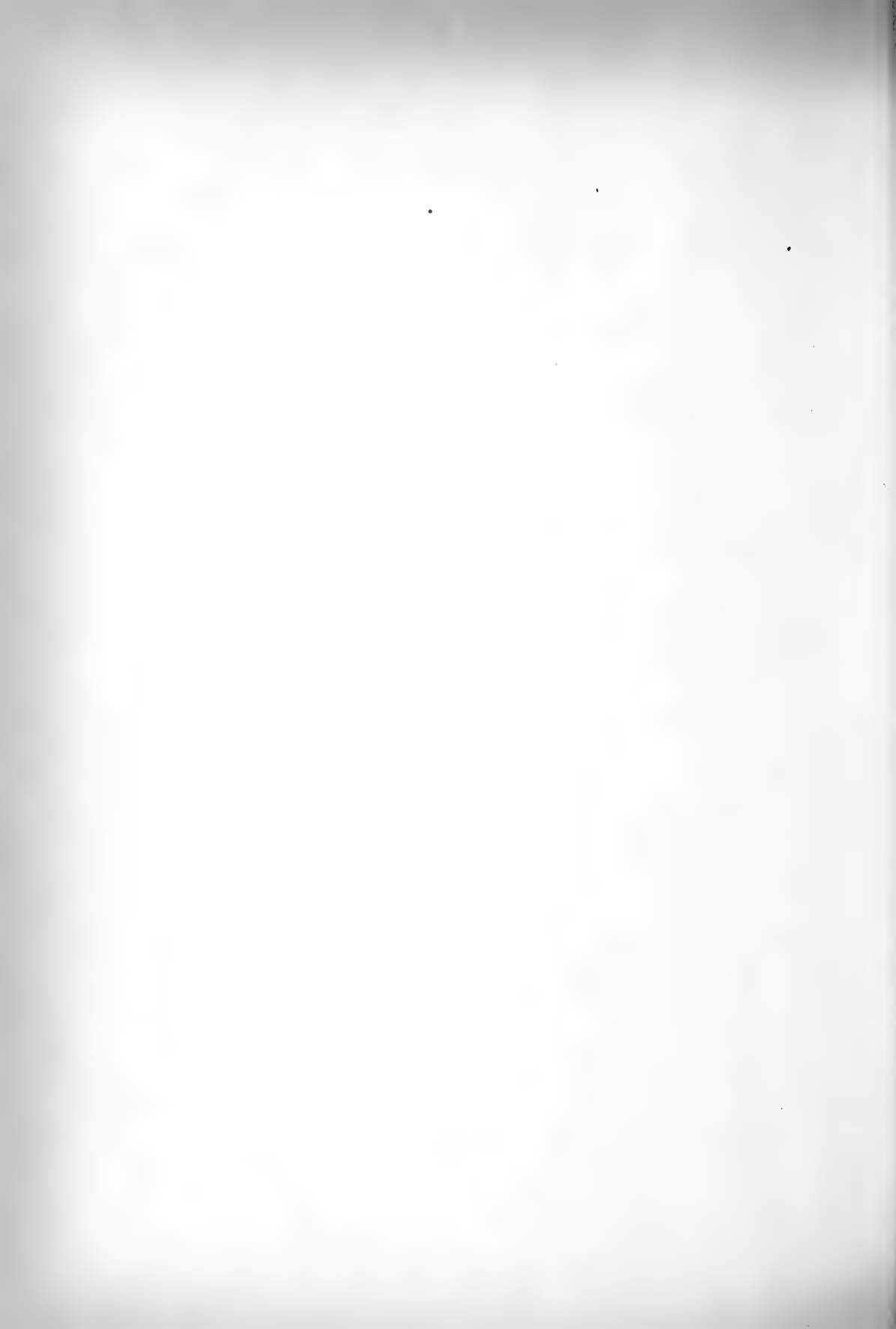
The ultra-violet absorption spectra of pyridine (I), 2-picoline (II), quinoline (III), quinaldine, quinaldinic acid and iso-quinoline have been measured in buffered aqueous solutions of known pH. In every instance the absorption at pH 4 differed from that at pH 7 in that the intensity of the long wave-length band was increased by a factor of approximately two and, except for I, II and III, was shifted from the red. This behaviour is attributed to the formation of the ion at pH 4.

The introduction of  $H^+$  into I, II and III affects equally the energies of the two molecular orbitals concerned in a transition, but this is not so with the other three compounds.

The method of ultra-violet absorption spectra is suited to the determination of pK values for pyridine type compounds.

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PART II

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# NITROGEN IN OIL SHALE AND SHALE OIL.

## X. NITRILES IN SHALE OIL.

By GEO. E. MAPSTONE, M.Sc., A.A.C.I., A.R.I.C., M.Inst.Pet.

*Manuscript received, April 10, 1949. Read, June 1, 1949.*

### INTRODUCTION.

The only nitrogen compounds that have yet been isolated and identified from shale oil are pyridine homologues, though pyrroles have also been identified as a class (Mapstone, 1948a). Apart from these, and the presence of possible traces of primary amines (Mapstone, 1948a), no other classes of nitrogen compounds appear to have been detected in crude shale oils. This is probably due to the difficulty of isolating and examining the weakly basic and non-basic nitrogen compounds from the oil, even though less than 20% of the nitrogen present in crude shale oil is sufficiently basic to be extracted by dilute acids. It is of interest that more than 20% of the nitrogen is not extracted even by concentrated sulphuric acid (Mapstone, 1948e).

A review of the pyrolytic reactions that may be involved in the carbonisation of oil shale to produce crude shale oil, suggested that nitriles may be present in the oil in small amounts (Mapstone, 1948c, 1948d). The work described in this paper was carried out in an attempt to detect nitriles as a class in crude shale oil.

### HYDROLYSABLE NITROGEN IN CRUDE SHALE OIL.

Previously, it had been found that the distillation of the oil with caustic soda solution required several hours before all the ammonia was distilled (Mapstone, 1945). This prolonged treatment would cause hydrolysis of any amides or nitriles, and the total ammonia evolved would be that from these sources, as well as that from free ammonia and ammonium salts initially present in the oil. At the same time, some of the lower boiling pyridine homologues present could be expected to distil along with the small amount of oil which came over with the ammonia and steam, and these would be recorded as ammonia. The original method was therefore modified, and the different factors examined in turn.

The proportion of oil distilling with the steam was reduced appreciably by using a fractionating column. In this respect a twelve pear column, although slightly more efficient than a four pear column, increased the time required for the distillation between two- and three-fold. By using a low heating rate, the fractionating column acted as a reflux condenser. Handling losses, etc., were greatly reduced by gently refluxing the oil with the caustic soda solution for a while, and then distilling off the ammonia with a fair amount of steam at a faster rate.

In the absence of an antifoaming agent, it was almost impossible to carry out a test. Cresylic acid was a very effective antifoaming agent, and better than amyl or butyl alcohols, which, though effective at the start, passed over with the steam during the distillation, so that serious foaming was sometimes experienced near the end of the test.

Between 50% and 60% of the tar bases present in the oil which distilled with the ammonia and water were extracted by the boric acid and titrated as ammonia. The oil distillate recovered from a series of tests using unwashed crude shale oil contained approximately 0.045% by weight of basic nitrogen.

Once the principle of the analytical method was established, a series of analyses was carried out, using the same sample of crude oil. The results obtained decreased steadily throughout the series from about 130 to 60 p.p.m. by weight of nitrogen in the oil. This decrease was shown to be most probably due to loss of free ammonia by the reduction of the hydrolysable nitrogen content of a fresh sample of oil from 132 to 55 p.p.m. by bubbling with air overnight.

#### EFFECT OF ACID WASHING ON HYDROLYSABLE NITROGEN.

Preliminary experiments indicated that, even in the absence of ammonia, the hydrolysable nitrogen content of the crude shale oil was reduced by washing the oil with dilute acids (Table I). A further series of experiments was therefore carried out by acid washing solutions of various nitriles and of oleamide in acetic acid-washed crude shale oil.

TABLE I.  
*Acid Washing Crude Shale Oil.*

Acid.	Amount of Acid.	Washing Time.	Water Wash.	Hydrolysable Nitrogen. (Parts per Million.)
Nil .. .. .	—	—	—	90
Acetic 5% .. ..	400 ml./l.	$\frac{1}{2}$ hour.	Nil.	56
Acetic 5% .. ..	400 ml./l.	$\frac{1}{2}$ hour.	500 ml./l.	72
Acetic 5% .. ..	400 ml./l.	16 hours.	Nil.	60
Acetic 5% twice ..	400 ml./l.	$\frac{3}{4}$ hour.	500 ml./l.	47
Acetic 25% .. ..	150 ml./l.	$\frac{1}{2}$ hour.	500 ml./l.	37
Acetic 25% twice ..	150 ml./l.	$\frac{3}{4}$ hour.	500 ml./l.	28
Acetic 25% .. ..	150 ml./l.	17 days.	500 ml./l.	26
Acetic glac. .. ..	10 ml./l.	$\frac{1}{2}$ hour.	2 × 500 ml./l.	56
Acetic glac. twice ..	10 ml./l.	$\frac{3}{4}$ hour.	2 × 500 ml./l.	53
Acetic glac. .. ..	10 ml./l.	16 hours.	2 × 500 ml./l.	53
Sulphuric 5% .. ..	400 ml./l.	1 hour.	Nil.	34
Sulphuric 5% .. ..	400 ml./l.	1 hour.	500 ml./l.	38
Sulphuric 5% .. ..	400 ml./l.	16 hours.	500 ml./l.	28
Sulphuric 10% .. ..	170 ml./l.	1 hour.	500 ml./l.	34
Sulphuric conc. .. ..	40 ml./l.	1 hour.	3 × 500 ml./l.	35

The results obtained (Table II) indicated that the most of any acetonitrile present was removed by the washing. As the molecular weight of the nitriles increased, the proportion extracted by the dilute acids generally decreased, although benzyl cyanide was the least extractable of the nitriles examined. Oleamide was several times as readily extracted as cetyl cyanide, a difference which appears due to the difference in the properties of the polar groupings rather than in the hydrocarbon chains.

By washing with 5% sulphuric acid and separating immediately, and then washing another portion of the sample and leaving it in contact with the acid overnight, it was hoped that some measure of the amount of hydrolysis occurring during the washing could be obtained. The results (Table II) suggested that there was little, if any, hydrolysis at the oil-acid interface.

TABLE II.  
*Effect of Acid Washing on Nitriles in Crude Shale Oil.*

Organic Cyanide Added.	Nil. p.p.m. N.	Acid Treatment.					
		250 ml./l. of 5% H <sub>2</sub> SO <sub>4</sub> then H <sub>2</sub> O.		250 ml./l. 5% H <sub>2</sub> SO <sub>4</sub> overnight then H <sub>2</sub> O.		50 ml./l. glac. HAc then 2 × 500 ml./l. of H <sub>2</sub> O.	
		p.p.m. N.	% Loss.	p.p.m. N.	% Loss.	p.p.m. N.	% Loss.
Unwashed oil .. ..	97	—	—	—	—	—	—
Washed oil .. ..	31	26	16	19	39	—	—
Benzyl .. ..	564	520	6	557	1	570	1
Methyl .. ..	1300	271	79	170	87	43	97
Butyl .. ..	248	145	42	180	27	138	44
Cetyl .. ..	41	34	17	31	24	37	10
Cetyl .. ..	94	81	14	78	17	85	10
Oleyl amide .. ..	776	188	76	216	72	253	67

#### MILD REDUCTION OF CRUDE SHALE OIL.

If the hydrolysable nitrogen compounds in the crude shale oil were nitriles, reduction of the oil should decrease or even eliminate them. Because it was neutral and would therefore not hydrolyse the nitriles during the reduction, aluminium amalgam was chosen as the reducing agent.

As a preliminary test, four litres of acetic acid washed crude shale oil were refluxed for eight hours with 121 grammes of amalgamated aluminium strip. The hydrolysable nitrogen contents of the washed oil, the reduced oil, and the reduced oil plus 1.6 ml./l. of aceto nitrile were determined, together with the effect of a mild acid wash. The results (Table III) indicate a significant reduction of the hydrolysable nitrogen content of the oil, and that the remaining compounds were more readily extracted with acid.

TABLE III.  
*Effect of Reduction of Oil by Aluminium Amalgam.*

Oil Treatment.	Nil.	Acid Treatment.					
		250 ml./l. 5% H <sub>2</sub> SO <sub>4</sub> then H <sub>2</sub> O wash.		250 ml./l. 5% H <sub>2</sub> SO <sub>4</sub> overnight then H <sub>2</sub> O wash.		50 ml./l. glac. HAc. then 2 × 500 ml. H <sub>2</sub> O.	
		p.p.m. N.	% Loss.	p.p.m. N.	% Loss.	p.p.m. N.	% Loss.
Washed crude oil ..	47	31	34	38	19	40	15
Washed crude oil re- fluxed over Al-Hg ..	29	16	45	12	59	18	38
Reduced crude oil plus some aceto nitrile ..	521	367	29	238	54	149	71

A further experiment was carried out in which a slow stream of air was passed through four litres of unwashed crude shale oil refluxing over aluminium



amalgam, and then through a solution of boric acid. Samples of the oil were withdrawn each four hours, and the hydrolysable nitrogen content determined. No ammonia was evolved during the progress of the reduction. After one sample of crude oil had been refluxed with the aluminium amalgam for 24 hours, some benzyl cyanide was added (5 ml. to 3.2 l.) and the refluxing continued. The results obtained (Table IV) showed that the hydrolysable nitrogen content of the oil was reduced appreciably by the treatment, and that the rate of reduction decreased with time. This is consistent either with decreasing activity of the amalgam or with the initial more rapid reduction of some of the more reactive hydrolysable nitrogenous compounds. The results after the addition of the benzyl cyanide were inconclusive.

TABLE IV.  
*Reduction of Hydrolysable Nitrogen by Aluminium Amalgam.*  
Results in p.p.m. of Hydrolysable Nitrogen.

Oil Sample.	Time Refluxed with Aluminium Amalgam.					
	Nil.	4 Hours.	8 Hours.	12 Hours.	16 Hours.	24 Hours.
(i) Unwashed crude oil	104	67	40	—	—	—
(ii) Unwashed crude oil	47	37	35	34	—	33
(iii) Crude oil from (ii) plus some added benzyl cyanide ..	101	99	98	—	96	—

The reduction of the nitriles should give rise to primary amines, and the detection of these in increased amounts in the crude shale oil after reduction with the aluminium amalgam would confirm the presence of nitriles in the oil. The 10 to 40 p.p.m. reduction in the hydrolysable nitrogen content of the oil obtained should be a measure of the amount of primary amine produced. This was far too small an amount of amines to be determined quantitatively, as the basic nitrogen content of the oil is of the order of one thousand times as much.

McKee claimed to have detected traces of primary amines in shale oil with nitrous acid (Mapstone, 1948a; McKee, 1925) and Horne, Finley and Hopkins obtained similar results using the carbylamine reaction (Mapstone, 1948a; Horne, Finley and Hopkins, 1938). Since the latter test seemed to be the better of the two, it was applied to samples of the crude shale oil which had been treated in various manners. Because of the very low amount of amine being sought, the samples were submitted to a jury of nine for comment. They were asked to classify the results as positive, possible, or negative, and no one was allowed to know either the history of any sample or any previous verdict until he had given his own decision.

The results of the tests (Table V) indicated a fair divergence in sensitivity of smell of the different "jurymen", but all knew the odour of carbylamine beforehand, and no one gave all results negative. The only sample on which the opinion was unanimous was that which had been washed with acetic acid, and which would, therefore, contain no basic compounds. The results suggest that refluxing the oil with aluminium amalgam did increase the primary amine content of the oil very slightly from a "possible" trace to a "probable" trace. Weathering the oil had little effect on the primary amine content, but refluxing with solid caustic potash or hydrolysis with caustic soda solution reduced it, which may have been due to the loss of volatile amines during the treatment.

TABLE V.  
Results of Carbylamine Test on Various Samples of Crude Shale Oil.  
(Summary of nine opinions.)

Shale Oil Sample.	Positive.	Possible.	Negative.
1. Fresh crude oil .. .. .	2	1	6
2. Fresh crude oil plus 0.1% aniline .. .. .	8	Nil	1
3. Crude oil weathered 2 years .. .. .	2	1	6
4. Crude oil refluxed over solid KOH .. .. .	Nil	2	7
5. Crude oil washed with acetic acid .. .. .	Nil	Nil	9
6. Crude oil refluxed 6 hours with Al-Hg .. .. .	2	6	1
7. Crude oil refluxed 18 hours with Al-Hg and then hydrolysed .. .. .	Nil	1	8
8. Crude oil plus 0.1% benzyl cyanide refluxed 6 hours with Al-Hg .. .. .	3	1	5
9. Crude oil plus 0.1% benzyl cyanide refluxed 18 hours with Al-Hg and hydrolysed .. .. .	4	3	2

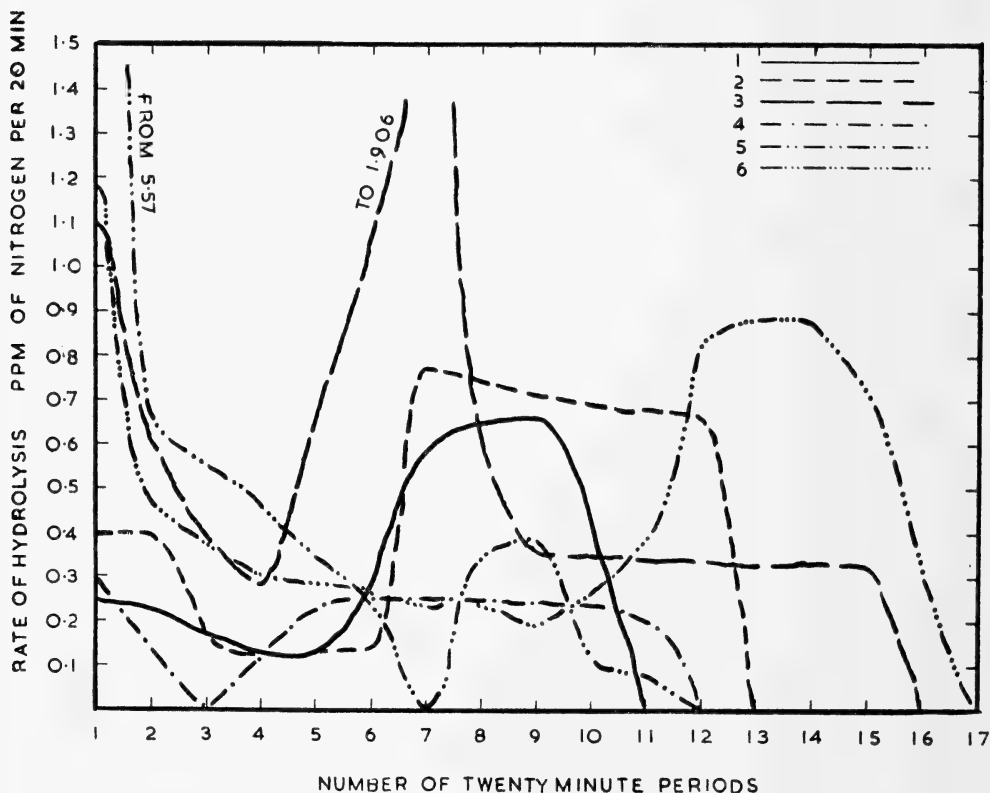


Fig. 1.

- Fig. 1.—Rate of Hydrolysis of some Crude Shale Oils.
- Sample No. 1. Acetic acid washed oil.  
 " No. 2. Acetic acid washed oil plus added benzyl cyanide.  
 " No. 3. Unwashed crude oil.  
 " No. 4. Unwashed crude oil after refluxing with Al-Hg for 20 hours.  
 " No. 5. Unwashed crude oil.  
 " No. 6. Weathered crude oil.

The aluminium amalgam reduction of the crude oil containing benzyl cyanide gave a definite increase in the primary amine content, which appeared to increase with time of refluxing.

#### RATE OF HYDROLYSIS OF CRUDE SHALE OIL.

Both amides and nitriles could exhibit most of the properties of the hydrolysable nitrogen components of the oil. A consideration of their properties suggested that it might be possible to distinguish between them by determining the rate of hydrolysis of the oil and of some amides and nitriles in solution in the oil, despite the small amount present.

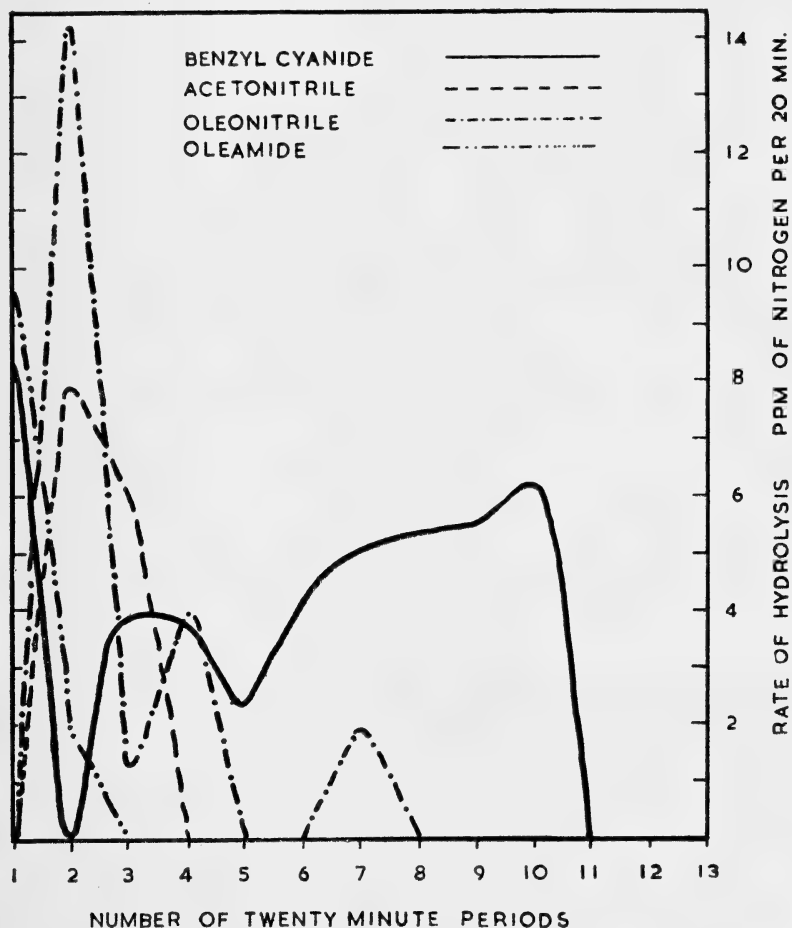


Fig. 2.

The results obtained with various samples of crude shale oil are presented graphically in Figure 1. With the samples of acid washed oil, the rate of ammonia evolution was not very high at first, and soon fell to a minimum which was followed by a pronounced peak or plateau in the rate curve. With the samples that had not been acid washed, the initial rate of ammonia evolution was much higher, but the peak or plateau was still observed in the latter part of the rate curve. This initially higher rate could be attributed to a combination of three factors: the possible presence of ammonium salts and the presence of

volatile tar bases in the crude shale oil together with the decomposition of some of the more readily hydrolysable compounds. All or part of these materials would be removed by the acid wash.

The results of the rate of hydrolysis of oleamide and some nitriles are presented graphically in Figure 2. The hydrolysis rate curves for the nitriles were of the same general type as those of the acid washed crude shale oil, by giving a pronounced minimum followed by a peak or plateau. Oleamide gave a rapidly decreasing rate curve without any indication of a subsequent peak.

Another inference drawn from this work was that the duration of the hydrolysis was a function of the amount of hydrolysable material present. This may be expected, as the rate of hydrolysis would be a function of the degree of contact between the oil and the caustic solution. Also, the rate of hydrolysis is obviously a function of the structure of the nitrile.

The significant difference in the hydrolysis rate curves for oleamide and for the nitriles suggests that the occurrence of a peak or plateau in the curve may be used as a tentative indication of the presence of nitriles in the oil. At present, no explanation can be given for the shape of the hydrolysis rate curve of the nitriles, though it appears that it may be due to the fact that the hydrolysis is a two-stage reaction in first giving rise to the amide. It is quite probable that some amides, as well as nitriles, may be present in the oil, but this method could not very well be employed to detect amides in the presence of nitriles.

#### FORMATION OF ORGANIC ACIDS ON HYDROLYSIS OF CRUDE SHALE OIL.

The results presented in Table VI show a fairly close correspondence between the amount of ammonia evolved on hydrolysis of the oil and the amount of organic acids formed at the same time. The discrepancies are relatively large, ranging from 20% to 50% of the amount of ammonia obtained, but the maximum difference was only 5.3 mg. of ammonia from 500 ml. of oil. Also, the necessarily involved method of isolation of the organic acids and the possibility of the presence of traces of esters in the crude oil, could tend to give high results, while any discrepancies in the determination of the ammonia would, if anything, tend to give low results. Since the acid obtained in each case was in excess of the ammonia liberated, the results can be interpreted with a reasonable degree of certainty as supporting the previous deduction that the hydrolysable nitrogen compounds present in crude shale oil are nitriles, and possibly some amides.

TABLE VI.  
*Organic Acids from the Hydrolysis of Crude Shale Oil.*  
(Results are expressed in mg. of ammonia as obtained from 500 ml. of acid washed oil.)

Sample No.	Ammonia.	Organic Acids.
A	7.9	13.2
B	10.4	12.3
C	10.7	13.2

#### SUMMARY.

From an examination of the effect of acid washing and of mild reduction on the hydrolysable nitrogen content of the crude shale oil, the rate of hydrolysis of the oil, and the determination of the amounts of organic acids formed by the hydrolysis of the oil, it appears that the hydrolysable nitrogen compounds

which are present in crude shale oil to the extent of 30-100 p.p.m. of nitrogen by weight are most probably nitriles. Traces of amides may also be present.

#### ACKNOWLEDGEMENTS.

The author wishes to acknowledge with thanks the technical assistance of E. J. Wolanin and R. S. Hayes, and the permission granted by the management of National Oil Pty. Ltd. for the publication of this paper.

#### EXPERIMENTAL.

##### *Determination of Hydrolysable Nitrogen.*

A measured volume (generally 50 or 100 ml.) of crude shale oil and 150 ml. of 10% caustic soda solution was charged into a long-necked flask of 500 to 750 ml. capacity, and 5 ml. of commercial cresylic acid or amyl or butyl alcohol added. The flask was then fitted with a four pear fractionating column fitted to a condenser, the delivery from which dipped below the surface of 50 ml. of 2% boric acid in a dropping funnel. The funnel was sealed and fitted with a bunsen valve (Meneghini, 1945) to reduce the danger of an accidental "suck back". Heating was commenced, and maintained at a sufficiently low rate for the liquid to boil in the flask, but for very little to distil, the fractionating column acting as a dephlegmator at almost total reflux. After an hour the rate of heating was increased, so that approximately 100 ml. of water were distilled during the next half hour. After the distillation had been completed, the lower aqueous layer of the distillate was separated, and the oil distillate washed with 25 ml. of ammonia-free distilled water. This was added to the separated boric acid solution, which was then titrated with 0.05 N sulphuric acid, using screened methyl orange as indicator (I.P., 1946). This separation step was necessary, as otherwise the oil interfered with the titration by extracting the methyl orange from the aqueous phase.

##### *Washing Crude Shale Oil with Glacial Acetic Acid.*

In order to extract free ammonia and the tar bases from a sample of crude shale oil before using it for other work, it was necessary to acid wash it. The washing was carried out by mixing thoroughly the required amounts of oil and glacial acetic acid (which was soluble in the oil), and adding the required amount of water. The dilute acid layer was then separated, and the oil washed with a further amount of water.

##### *Carbylamine Test on Crude Oil.*

This test was carried out by boiling 10 ml. of the crude shale oil with 0.5 ml. of chloroform and 1.0 ml. of 10% caustic soda solution. All samples were prepared and, when cool, were submitted together to the "jury" for smelling.

##### *Determination of the Rate of Hydrolysis of Crude Shale Oil.*

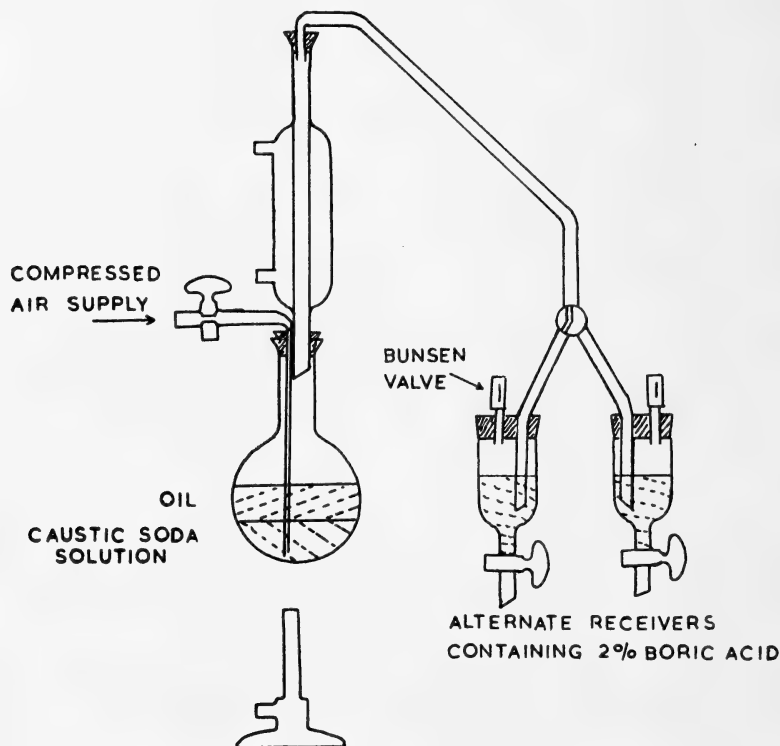
Crude shale oil (250 ml.), 10% caustic soda solution (300 ml.), and cresylic acid (10 ml.) were charged into a 750 ml. bolt-head flask fitted up as in Figure 3. The air flow was controlled so that three bubbles per second escaped through the boric acid solution in the receiver, and heating was commenced. The current of air served the dual purpose of carrying off the ammonia as it was liberated, and of mixing the oil and the caustic soda solution and eliminating bumping during the boiling. Zero time for the hydrolysis was taken as the time the mixture started to boil, as shown by the return of liquid condensate from the condenser. From that time, the air stream was diverted to alternate receivers containing boric acid, at 20 minute intervals. After the air had been diverted from a receiver, the aqueous layer was carefully separated from any oil that had distilled, and titrated with 0.05 N sulphuric acid, using screened methyl orange as the indicator. This process was repeated until at least three consecutive titrations indicated that no ammonia had been evolved during the period. The experiments were carried out in duplicate and the results averaged.

The rates of hydrolysis of the oleamide and the nitriles were determined by adding some of the compound to 250 ml. of the oil which had been completely hydrolysed. Equal amounts were added to each of two samples of oil, and the rates of hydrolysis of the two samples averaged.

*Formation of Organic Acids on Hydrolysis of Crude Shale Oil.*

A quantity of the crude shale oil to be tested was acid washed to remove ammonium salts and volatile tar bases, which could interfere with the analysis, and then washed several times with hot water to remove any residual traces of acid. The final washings were neutral to alkali blue.

Five hundred ml. of the washed oil were refluxed with 100 ml. of 10% caustic soda solution and 5 ml. of cresylic acid, in the same apparatus as used for the determination of the rate of hydrolysis, so that it was possible to determine when the hydrolysis was complete, as well as the total amount of ammonia evolved. The lower caustic soda layer was indistinguishable from the oil layer, except in bright sunlight or ultra-violet light, when the oil fluoresced a strong green.



APPARATUS FOR DETERMINATION OF RATE OF HYDROLYSIS OF OIL

Fig. 3.

The two layers were separated, and the oil washed with two 50 ml. portions of hot water. The combined caustic extract and washes were acidified with concentrated hydrochloric acid, and extracted with 100 ml. of gasoline. The gasoline was washed twice with 100 ml. portions of distilled water before the total (organic) acidity was determined by I.P. Method 1/46 (I.P. 1/46, 1948).

Before hydrolysis, the organic acid content of the crude oil was nil. A blank test indicated that the 5 ml. of cresylic acid added to act as an antifoaming agent during the hydrolysis contained organic acids equivalent to 0.73 mg. of ammonia. This was allowed for in calculating the amount of organic acids formed by the hydrolysis of the oil.

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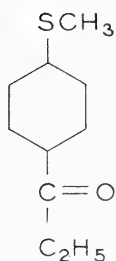
## SYNTHETIC SEX HORMONES.

### PART II. THE PINACOLS AND PINACOLONE OF *p*-METHYLMERCAPTOPROPIOPHENONE, AND THE PREPARATION OF DITHIODIENESTROL DIMETHYL ESTER.

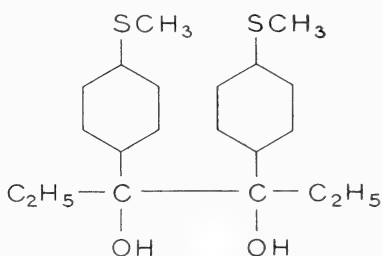
By G. K. HUGHES, B.Sc.  
and E. O. P. THOMPSON.

*Manuscript received, April 6, 1949. Read, June 1, 1949.*

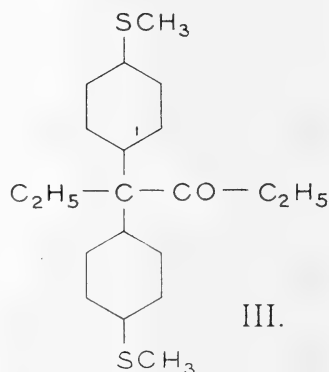
The successful dehydration of the pinacols from *p*-hydroxyacetophenone by Dodds, Goldberg, Lawson and Robinson (1939) to the corresponding butadiene, suggested the possibility of dehydrating the *pinacols*, II, derived from *p*-methylmercaptopropiophenone, I, to the sulphur analogue of dienestrol dimethyl ether IV. With potassium bisulphate or acetyl chloride, only the



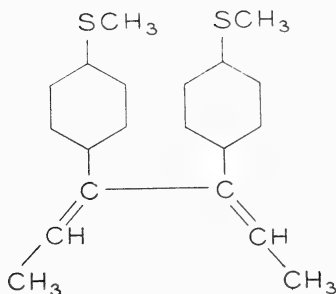
I.



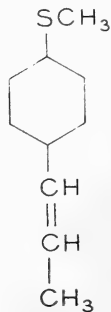
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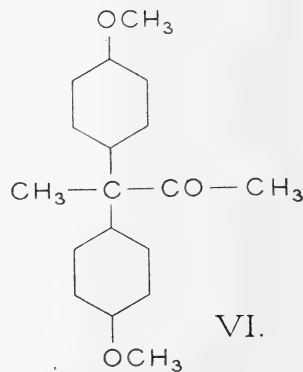
III.



IV.



V.



VI.

pinacolone III was isolated. However, both the *meso* and *dl* forms of the pinacol gave with a mixture of acetic anhydride and acetyl chloride (cf. Dodds *et al.*, 1939), along with the pinacolone, a white crystalline solid which is the *hexadiene* IV.



Several methods of preparing the pinacols, II, were studied. Electrolytic reduction of the ketone, in an aqueous alcoholic solution containing potassium acetate, with a lead cathode as described by Price and Mueller (1944) gave a mixture of the pinacols which were separated readily owing to their different solubilities.

The high melting isomer is moderately soluble in hot benzene or alcohol and almost insoluble in ether, whereas the low melting pinacol is readily soluble in most organic solvents and can only be crystallized with difficulty from petroleum ether.

The method of Bachmann (1933) using sodium amalgam with alcohol in ether-benzene solution gave a good yield of the pinacols. With diaryl ketones this method gives a quantitative yield of the corresponding hydrol, the highly coloured sodium ketyl radicals being formed as intermediates. Possibly the reduction of *p*-methylmercaptopropiophenone proceeds by a different mechanism as no marked colour was developed. Magnesium and magnesium iodide which Gomberg and Bachmann (1927) introduced for the preparation of pinacols from diaryl ketones in quantitative yield (coloured iodomagnesium ketyl radicals being formed in the reaction) gave only small yields (8%) of the high melting pinacol, an olive green colour accompanying the reaction. However, Bachmann and Ferguson (1934) reported poor yields of pinacols from diaryl ketones containing alkoxyl groups with this reagent.

Aluminium amalgam and alcohol as used by Newman (1940) gave a fair yield of the pinacols.

Zinc dust and acetic acid used by Bachmann and Ferguson (1934) for the preparation of pinacols from diaryl ketones gave no detectable amounts of the pinacols but some thioanethole, V, was formed due to the easy dehydration of the hydrol as described by Hughes and Thompson (1948).

The pinacols were identified by oxidation with lead tetra-acetate as used by Price and Mueller (1944). The low melting pinacol was rapidly oxidized to the ketone, I, which was isolated quantitatively as the phenylhydrazone. The high melting isomer was oxidized slowly and using excess lead tetra-acetate the sulphoxide of *p*-methyl mercaptopropiophenone was isolated as its phenylhydrazone.

Attempts to identify the ketone, I, by selective oxidation with selenium dioxide followed by periodic acid, to *p*-methylmercaptobenzoic acid gave instead the sulphoxide of this acid. Mel'nikov (1935) had previously reported the oxidation of sulphides to sulphoxides and sulphones by selenium dioxide.

Attempts to esterify the high melting pinacol with acetic anhydride and pyridine, and by the Schotten Baumann method with benzoyl chloride, were unsuccessful, the pinacol being recovered unchanged.

Both pinacols were readily rearranged with acetic anhydride and sulphuric acid (Price and Mueller, 1944) and iodine and acetic acid (Gomberg and Bachmann, 1927); the latter method gave the better yield.

The pinacolone obtained would not give a dinitrophenylhydrazone or an oxime using the most stringent conditions of Bachmann and Barton (1938). This agrees with the observation of Sisido and Nozaki (1948) on the oxygen analogue.

Price and Mueller (1944) using the somewhat similar pinacolone 2 : 2'-di-(*p*-methoxyphenyl)-butan-3-one VI did obtain an oxime. Heating the pinacolone III, with hydroxylamine hydrochloride and alcohol in a sealed tube for six hours at 160° C. gave no oxime or rearranged product the pinacolone being recovered unchanged. Under similar conditions, Feith and Davies (1891) obtained *N*-acetyl-mesidine from acetomesitylene which under normal conditions will not form an oxime.

The structure of the pinacolone was assumed to be III, by analogy with the pinacolone obtained by Wessely, Kerschbaum, Kleedorfer, Prillinger and Zajic (1940). It gave a positive test for an enolizable hydrogen atom with *m*-dinitrobenzene and alkali in pyridine solution.

A 25% methyl alcohol solution of caustic potash did not split the pinacolone after eighty hours' refluxing.

This structure was confirmed by oxidation of the pinacolone or its sulphone with chromic acid to *p*:*p'*-dimethylsulphonylbenzophenone.

#### EXPERIMENTAL.

For the preparation of *p*-methylmercaptopropiophenone, see Hughes and Thompson (1948).

##### *Electrolytic Reduction.*

The apparatus consisted of a porous pot (fitted with a condenser) which contained the catholyte immersed in a 40% aqueous solution of potassium carbonate. The cathode was made of lead foil 100 sq. cm. in area, and the catholyte was a solution of *p*-methylmercaptopropiophenone (55 g.) in alcohol (125 ml.) to which water (50 ml.) containing potassium acetate (28 ml. saturated solution) was added. The electrolysis was carried out at reflux temperature using a current density of 0.02 amp./sq. cm., and after passing 120% theoretical current the mixture was poured into water.

The crude material was dissolved in hot alcohol, and on cooling the high melting pinacol separated and was completely removed by concentration of the mother liquors.

The crude high melting pinacol (10 g.) on repeated recrystallization from ethyl alcohol gave white crystals (8 g.) m.p. 168° C.

Found: C, 65.76; H, 7.19%. Calculated for  $C_{20}H_{26}O_2S_2$ : C, 66.23; H, 7.23%.

After removal of the alcohol from the mother liquors the residue was repeatedly recrystallized from petroleum ether (60–80°) to give the other pinacol m.p. 93° C.

Found: C, 66.00; H, 7.31. Calculated for  $C_{20}H_{26}O_2S_2$ : C, 66.23; H, 7.23%.

##### *Reduction with Sodium Amalgam.*

To the ketone (10 g.) dissolved in a mixture of anhydrous ether (70 ml.), benzene (70 ml.) and alcohol (7 ml.) was added sodium amalgam (167 g., 2%) and the mixture shaken in a tightly stoppered bottle for two hours.

No marked change in the initial yellow colour was noticed, and the solution gradually became cloudy as the high melting pinacol separated out.

The mixture was poured into water, acidified, and after separation of the organic layer extracted three times with hot benzene. The combined organic extracts were washed with water and the solvents removed under reduced pressure. The residue was mixed with ether and the insoluble pinacol (3.1 g.) filtered off. Evaporation of the ether followed by recrystallization from petroleum ether (60–80°) gave the other pinacol, m.p. 93° (3.9 g.).

The crude mixture of pinacols after removal of solvents may be rearranged with acetic acid and iodine to give the pinacolone (6 g.).

On the basis of yields obtained with pure pinacols this indicates at least 75% yield of pinacols.

Distillation of the crude pinacols under high vacuum gave no pinacol but a mixture of thioanethole V, ketone I and pinacolone III.

The pinacolone probably results from the effect of traces of acid and the ketone and thioanethole from disproportionation of the pinacols into ketone and hydrol, the latter being readily dehydrated.

##### *Reduction with Aluminium Amalgam.*

The ketone (30 g.) in absolute alcohol (300 ml.) and benzene (200 ml.) was treated with aluminium amalgam, prepared from previously etched foil (12 g.) and mercuric chloride (0.5 g.) and the mixture refluxed twenty-four hours. When poured into water and worked up in the manner described for the sodium amalgam method, the pinacols, m.p. 167° (10 g. crude) and m.p. 93° (8 g. crude) were obtained.

*Reduction with Magnesium and Magnesium Iodide.*

Magnesium iodide prepared by refluxing excess magnesium turnings (2.5 g.), iodine (7 g.) in a mixture of ether (18 ml.) and benzene (25 ml.) was shaken with the ketone (9 g.) in benzene (8 ml.). An olive green colour developed and after shaking three hours the liquid was decanted into water, acidified with hydrochloric acid and extracted with benzene. The organic extracts were washed with water and the solvents removed under diminished pressure. Ether was added to the oil and allowed to stand overnight, when a small amount of high melting pinacol (0.8 g.) separated. No pinacol could be obtained from the ether solution which consisted of unchanged ketone. Rearrangement of the residue after removal of the high melting pinacol gave oils from which no pinacolone could be crystallized.

*Reduction with Zinc and Acetic Acid.*

The ketone (10 g.) in glacial acetic acid (100 ml.) was treated with zinc dust (20 g.) during the course of two weeks of standing at room temperature. When the solution was decanted into water a semi-solid mixture was obtained which when filtered gave a solid, and an oil with a strong aniseed odour.

The solid was unchanged ketone identified by mixed melting point. The oil was distilled under reduced pressure to give thioanethole (2 g.) b.p. 143° at 25 mm. (approx.) and *p*-methylmercaptopropiophenone, b.p. 190° at 25 mm. (approx.).

*Oxidation of the Pinacols with Lead Tetraacetate.*

The low melting pinacol (1 g.) was suspended in glacial acetic acid (5 ml.) and the theoretical amount of lead tetraacetate (1.25 g.) was added. When both reactants had dissolved, the ketone was separated as the phenylhydrazone by addition of phenylhydrazine (1 ml.) in glacial acetic acid (3 ml.) and shaking thoroughly with the slow addition of water (2 ml.).

The phenylhydrazone after washing was recrystallized several times from alcohol, m.p. 84°. A mixed melting point with an authentic specimen prepared from *p*-methylmercaptopropiophenone showed no depression.

The derivative decomposed after several hours, and therefore was not analysed.

The high melting pinacol when treated in this way gave no phenylhydrazone unless excess lead tetra-acetate (2.5 g.) was used when a yellow compound was obtained m.p. 175° after several recrystallizations. It did not depress the melting point of an authentic specimen of the phenylhydrazone of the sulfoxide of the ketone.

The phenylhydrazones of the sulfoxide (m.p. 176°) and sulphone (m.p. 150°) of *p*-methylmercaptopropiophenone were prepared in the usual manner from the sulfoxide and sulphone and were recrystallized from alcohol.

*Oxidation of p-Methylmercaptopropiophenone with Selenium Dioxide and Periodic Acid.*

The ketone (10 g.), selenium dioxide (12.5 g.) and dioxane (60 ml.) were refluxed four hours during which black selenium separated. The solution was decanted and the excess dioxane removed under reduced pressure. The residue was extracted with ether, the ether removed, water (50 ml.), potassium periodate (12.8 g.) and concentrated sulphuric acid (1.5 ml.) added and the mixture shaken and stood overnight. The solid material was filtered off, treated with caustic soda and filtered. The filtrate was acidified and the residue recrystallized from water to give a pale yellow solid (2.2 g.) m.p. 229°, which did not depress the melting point of an authentic specimen of *p*-carboxyphenyl methyl sulfoxide.

The sulfoxide m.pt. 233° and sulphone m.pt. 267° of *p*-methylmercaptobenzoic acid were prepared from the acid by oxidation in the usual way, in acetone and acetic acid solution respectively, with hydrogen peroxide (30%). They both recrystallized from water in white crystals.

Found: C, 51.17; H, 4.50; S, 17.25%. Calculated for  $C_8H_8O_3S$ : C, 52.12; H, 4.38; S, 17.4%.

Found: C, 47.26; H, 3.94; S, 15.75%. Calculated for  $C_8H_8O_4S$ : C, 47.96; H, 4.03; S, 16.02%.

*Pinacolone Rearrangement.*

The pinacol (10 g.) was suspended in acetic anhydride (50 ml.) and concentrated sulphuric acid (1.25 ml.) added drop by drop. A purple colour was obtained which faded to a light brown and all the solid dissolved. The solution was poured into water and neutralized with sodium carbonate when the oil obtained gradually solidified.

The solid was recrystallized from alcohol to give 2 : 2-di-(*p*-methylmercaptophenyl)-hexane-3-one m.p. 90–95°.

Concentration of the mother liquors gave a small amount (0.2 g.) of white solid m.p. 150°. Further concentration gave more pinacolone VI. The pinacolone fractions on repeated recrystallization from alcohol had m.p. 95° C.

Found : C, 69.4 ; H, 6.90%. Calculated for  $C_{20}H_{24}OS_2$  : C, 69.69 ; H, 7.02%.

The small amount of impurity on recrystallization had m.p. 157°.

Found : C, 65.3 ; H, 6.8%. This was possibly the isomeric pinacolone.

The yield was slightly better, 70%, with the high melting pinacol, the other isomer giving 60% yield.

Alternatively the pinacol (5 g.) was refluxed with acetic acid (25 ml.) and a crystal of iodine for several hours and then poured into water and neutralized. When recrystallized both pinacols gave the pinacolone (3.8 g.) m.p. 95° C. No other product was isolated in this case.

*Oxidation of the Pinacolone.*

*Potassium Permanganate. Formation of the Sulphone.* The pinacolone (1 g.) in glacial acetic acid solution was treated slowly with a solution of potassium permanganate (1.37 g.) in water (40 ml.). After addition was complete the solution was decolorized by sulphur dioxide. A white precipitate remained which when recrystallized from methanol gave the sulphone (0.68 g.) m.p. 149.5° C.

Found : C, 57.8 ; H, 6.05 ; S, 15.36%. Calculated for  $C_{20}H_{24}O_5S_2$  : C, 58.8 ; H, 5.92 ; S, 15.7%.

The sulphone was also obtained by oxidation with hydrogen peroxide solution (30%) in acetic acid solution at 100° C.

*Chromic Acid.* The pinacolone (1.15 g.) or sulphone (2 g.) was dissolved in glacial acetic acid and chromic acid crystals (2 g.) together with concentrated sulphuric acid (1.3 ml.) added and the mixture refluxed for thirty minutes. The reaction mixture was poured into water and almost neutralized with sodium carbonate. A solid separated which was filtered off, washed with water and recrystallized from water, m.p. 236–237° C.

The compound was *p* : *p*-dimethylsulphonyl-benzophenone.

Found : C, 53.0 ; H, 4.23 ; S, 18.56%. Calculated for  $C_{15}H_{14}O_5S_2$  : C, 53.2 ; H, 4.17 ; S, 19.0%.

*Dithiodienestrol Dimethyl Ether.* The pinacol (5 g.) was refluxed with acetyl chloride (6 ml.) and acetic anhydride (9 ml.) for thirty minutes and poured on to ice. The semi-solid material recrystallized from alcohol to give a mixture of pinacolone and diene (3 g.) m.p. 80° C. When taken up in alcohol and cooled slowly the hexadiene (0.7 g.) m.p. 125–133° crystallized out and was carefully filtered off, the pinacolone (2 g.) m.p. 85–93° crystallizing in the receiver.

Repeated recrystallization of both fractions gave the pinacolone (1.3 g.) m.p. 95° C., and the dithiodienestrol dimethyl ether (0.4 g.) m.p. 141°.

Found : C, 72.8 ; H, 6.87 ; S, 19.76%. Calculated for  $C_{20}H_{22}S_2$  : C, 73.6 ; H, 6.75 ; S, 19.6%.

## ACKNOWLEDGEMENT.

The authors gratefully acknowledge the assistance of Miss J. Fildes for the semimicro-analyses recorded in this paper.

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# METALLOGENETIC EPOCHS AND ORE REGIONS IN THE COMMONWEALTH OF AUSTRALIA.\*

By W. R. BROWNE, D.Sc.

With one Table and six Text-figures.

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## INTRODUCTION.

The wise old Hebrew prophet well knew the value of the inspiration and encouragement to be got from a contemplation of the illustrious past when he counselled his countrymen: "Look ye unto the rock whence ye are hewn, and the hole of the pit whence ye are digged; look unto Abraham your father and to Sarah that bare you." It was doubtless with the same thought in mind that the Royal Society of New South Wales ordained that the memory of that great citizen and scientist, Rev. W. B. Clarke, who may be regarded as its second founder, should be kept green by the delivery of an annual lecture dedicated to his name. I am very proud and honoured to have been asked by the Council to be the lecturer for this year, for I have long been an ardent admirer of the "father of Australian geology", of his geological enthusiasm, scientific insight, tireless energy, single-minded devotion to duty and uncompromising championship of what he was convinced was right. The pioneer geological work that he accomplished in the face of many obstacles must ever be an inspiring influence to geologists in this country.

Like his successors, David and Andrews, in the same field of investigation, Clarke combined an ardent love of geology for its own sake with a strong determination to apply his knowledge for the material advancement of his country. The implied recognition of the twofold character of geology is apt to be obscured alike by those who think of it simply and solely as a means to material gains and by those rare souls whose thoughts never stray from the pursuit of the so-called academic aspects of their studies. Only in so far as it holds a proper

\* The Clarke Memorial Lecture delivered to the Royal Society of New South Wales, June 16, 1949.

balance between the cultural and the utilitarian can geological science in this country hope to command the respect and attention that it merits and make the progress that it should.

For my lecture to-night I have chosen a theme which, while strictly speaking in the realm of pure geology, yet should hold some interest for the economic geologist, since the study of ore-deposits stands to gain from every attempt to arrange our knowledge in orderly fashion. From time to time there have been papers written and addresses given on the questions of metallogenetic epochs and ore provinces in various parts of the Commonwealth and in the continent as a whole. One thinks particularly of papers by E. S. Simpson and E. C. Andrews, by Waterhouse, Stillwell and Ball, and of the more recent work of E. S. Hills and Austin Edwards and the presidential addresses of Jones in Queensland and Prider in Western Australia.\* While deriving much from all this earlier work, my present intention is chiefly to analyse our information about the ore-deposits of Australia in the setting provided by an increased knowledge of the epochs of tectonic and igneous activity. The result must be regarded merely as a progress report and an interpretation, some part of which is bound later to be rejected and some to be modified.

If we were to consider ore-deposits in a very comprehensive way so as to include those of detrital or otherwise derivative character, we could recognise an almost endless succession of ore epochs, which would include the time of deposition of the very important pre-Cambrian sedimentary iron ores of Western Australia and South Australia, the Tertiary periods during which our laterites and bauxites and our alluvial gold and tin deposits were formed, and the Quaternary epochs marked by the concentration of the very valuable zircon and rutile deposits at various places along the coast of eastern Australia and Tasmania. We shall, however, confine our attention to the primary ore-deposits, that is to say, those deposits of ores which are related to the igneous rocks.

#### GEOGRAPHICAL DISTRIBUTION OF ORE-DEPOSITS.

Australia may be broadly divided into three great topographic regions (Fig. 1): (a) the Great Western Plateau, including the pre-Cambrian shield and stretching over Western Australia, the greater part of Northern Territory and much of South Australia, with extensions into the far west of Queensland and New South Wales; (b) the Central-Eastern Lowlands, made up largely of the Mesozoic sediments of the Great Australian Artesian Basin and the Cainozoic deposits of the Murravian Basin; and (c) the Eastern Highlands belt, composed mainly of Palæozoic rocks and occupying much of eastern Queensland and New South Wales, the greater part of Victoria and virtually all of Tasmania.

The primary ore-deposits are confined to the first and third regions, wherein the rocks have been folded again and again and invaded by igneous magmas, most of which were ore-carriers. The strata of the second region are level-bedded, and their deposition has been unaccompanied by volcanic activity on a large scale. There are also in the plateau regions marginal areas of barren, horizontal or gently folded strata, such as the Desert Basin and the North-West and South-West Basins in Western Australia, the Nullarbor Plain, the areas occupied by Mesozoic rocks in all the States and the great Sandridge Deserts. Some of these form lowlands and some highlands, and on the other hand there are lowlands, particularly in the coastal belts, composed of intensely folded ore-bearing rocks. Nevertheless, broadly speaking, the highland and lowland divisions of Australia have not merely a tectonic and structural but also a considerable economic import.

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\* See list of references.

The precise conditions of deposition of the Older pre-Cambrian rocks of the Great Western Shield we do not know ; but the Upper pre-Cambrian and Cambrian rocks were laid down in a great median basin of deposition including at least two elongated troughs, one running north and south in South Australia, the other east and west in Central Australia, partly on the site of the Macdonnell Ranges. In the first trough sediments to a maximum thickness of 12 or 15 miles were deposited before it was extinguished by folding of its strata. The Eastern Highlands belt was the site of the great Tasman Geosyncline, wherein sinking and deposition alternated with folding and plutonic injection throughout Palæozoic and Mesozoic time. The geosynclinal strata—chiefly marine—and their associated volcanic rocks became hosts for the metalliferous ores brought in contemporaneously with volcanic activity or introduced with the formation of plutonic bathyliths during the orogenic epochs.



Fig. 1.—Topographic Regions of Australia.

- (a) The Great Western Plateau.
- (b) The Central-Eastern Lowlands.
- (c) The Eastern Highlands Belt.

The blanketing effects of the unfolded post-Palæozoic beds are such that any ore-deposits in the underlying pre-Cambrian and Palæozoic rocks are hidden away as securely as if they did not exist. There is little doubt that ores are present in these old foundation-rocks, but they are at an extreme depth of at least 7000 feet in south-eastern Queensland and more than 5000 feet in the Murravian Basin. There is some reason to believe that the Cretaceous rocks of the Great Artesian Basin once encroached upon the highlands farther than at present, and that the rich ore-deposits of, for instance, Cloncurry in Queensland and Broken Hill and Cobar in New South Wales, have been revealed to us through erosion of the sediments of the Cretaceous epicontinental sea that covered the site of the Great Artesian Basin. Even in known ore-bearing areas a few inches of sand and soil can most effectively conceal the presence of metalliferous rocks,



but nowadays some of the hidden deposits are being detected by geophysical and geochemical prospecting.

#### RELATION OF ORES TO IGNEOUS ROCKS.

Geologists are not unanimous as to the exact origin and mode of emplacement of ores of the economic metals, but it is a matter of general agreement that they are somehow genetically related to magmas or igneous emanations which ascend from the deeper layers of the earth's crust and come to rest at depth or are ejected on to the surface. The question whether the ore-minerals were original and essential constituents of the magma, or were present in the invaded rocks, ingested by the ascending fluids and later regurgitated, as it were, does not greatly concern us; neither need we discuss the much debated problem of the origin of granite, with which so many ore-deposits are connected. All we are considering at the moment is the association of ore-deposition with the formation of igneous rocks at different geological epochs, which is far too common and widespread a phenomenon to be of other than genetic significance.

Some of our primary ores are in close and apparently genetic relation to volcanic lavas. For instance, masses of native copper were found in andesite of Devonian age in the Keelbottom River (Queensland), and there is reason to suppose that ore-mineral and host-rock are related. The small deposits of native copper in amygdales in the Permian trachybasalts on the South Coast of New South Wales are clearly comagmatic with the lavas, though doubtless the result of decomposition of cupriferous ferromagnesian minerals by deuteric solutions and subsequent deposition. It has been suggested that the silver-lead ores of Narlarla in West Kimberley (W.A.) are related to neighbouring volcanic plugs of Tertiary leucitic rock, and the quartz-veins containing gold, silver-lead and copper among the Upper pre-Cambrian Nullagine beds in the Pilbara district of Western Australia are considered to be comagmatic with the contemporaneous acid and basic lavas, while the gold of Cracow (Queensland) is thought by Denmead to have been introduced by andesitic magma in Mesozoic time.

The presence of ore-deposits in lavas may, however, be purely fortuitous, and it is probably so where gold is found in the Cambrian lavas or "diabases" of Heathcote (Victoria) and in the sheared Silurian andesites of Forbes, Blayney and Lucknow (N.S.W.).

Association of ores with hypabyssal intrusions, though far from common, is not unknown. In Western Australia there are many deposits of copper, lead, zinc and silver connected with basic dykes which have been variously assigned a late pre-Cambrian and a Palæozoic age but which may in fact belong to a number of different epochs. The copper of Blinman in the Flinders Ranges and other places in South Australia may have been introduced with certain basic dykes and other minor intrusions of Cambrian age. At Walhalla in central-eastern Victoria gold is closely associated with a swarm of dykes whose compositions range from intermediate to ultrabasic. On a much smaller and purely uneconomic scale are the auriferous pyrites of Mesozoic (?) quartz-dolerites and the gold associated with Tertiary (?) syenite-porphyrries in Tasmania. The copper and gold deposits of Cobar (N.S.W.) seem to be proximately related to intrusions of quartz-porphyry, but these are in their turn probably comagmatic with the granites cropping out at a distance of about 25 miles from the town.

It is clear that as with the volcanic rocks it may be hard to establish the existence of a genetic relation between ores and hypabyssal intrusions, since the jointing, cracking and shearing or faulting to which such rocks are liable may provide channels for ore-solutions not directly or at all connected with them.

By far the largest proportion of ore-deposits in the Commonwealth appear to be related to plutonic intrusions. They may be direct crystallizations or segregations of early-formed minerals, such as the chromite, platinum and osmiridium of the ultrabasic rocks, but for the most part they are of late deposition, crystallized in late differentiates or from late-magmatic or post-magmatic solutions, and chiefly in association with acid and intermediate rock-types. It is difficult to relate specific ore-minerals to specific rocks, but there is some evidence in the Commonwealth suggesting that gold accompanies granodiorite and copper and iron quartz-monzonite, while tin, tungsten, molybdenum, bismuth and antimony ores are of course found in general with the most acid types of granite. On the other hand examples have been reported of a zonal arrangement of ores around the margin of a bathylith according to the temperatures of formation, as at Heemskirk and other places in Tasmania and at Wolfram Hill in North Australia. In such circumstances the dominance of a particular metal in the ore-deposit is largely a function of the depth of erosion of the *terrain* or the distance from the edge of the intrusion.

The contention has been put forward that it is not necessarily correct to assume that a given primary ore-deposit is related to a neighbouring plutonic intrusion where the two are not in visible connexion. But around many bathyliths the normal contact-areole may have a surface-width of as much as a mile or more, and the deposition of relatively low-temperature ore-minerals from mobile magmatic solutions under pressure could surely have extended far beyond this limit. In any case the visible boundaries of its outcrop are not necessarily indicative of the underground extension of a bathylith, and the occasional presence of feldspar and tourmaline in ore-bearing quartz-veins sufficiently attests their magmatic origin even when they cannot be traced into pegmatites.

Ores are seldom monometallic, and complex types are known in which quite a number of metals are of approximately equal importance, but it is probably true that in the majority of instances one or a few metals are dominant or predominant.

#### EPOCHS OF IGNEOUS ACTIVITY AND METALLOGENESIS.

From the close connexion between ore-deposition and plutonic invasion it naturally follows that the great epochs of folding and plutonic invasion were also metallogenetic epochs. The bathyliths belong, broadly speaking, to two types, the synchronous or syntectonic and the subsequent or epitectonic. Opinions are divided as to the mode of emplacement of these, but the view is widely held that the first were formed largely through a process of transformation *in situ* of original sedimentary rocks by granitizing fluids, and that those of the second type represent the consolidation of bodies of liquid magma. However that may be, in the Commonwealth the synchronous type of bathylith was characteristic of the earliest known pre-Cambrian diastrophism, and of the late Ordovician and late Silurian orogenic epochs in eastern Australia. In general the other bathyliths are of subsequent type, though it would appear that some of those of late Middle pre-Cambrian age are synchronous. With both types ore-deposits are found to be associated.

Other possible metallogenetic epochs coincide with the times of injection of minor intrusions or with episodes of vulcanism, but, as already pointed out, these were not very important in Australia, and it can be said that with the vast majority of lava-flows and minor intrusions there have been found no signs of ore-deposits whatever. On the other hand the ores whose connexion with plutonic intrusions—bathyliths or stocks—is reasonably certain are legion.

All the forms of igneous activity referred to are related to geosynclinal deposition and deformation, but the volcanic and the hypabyssal may also be quite independent of it and be purely terrestrial in character.

In the geological record of the Commonwealth it is possible to discern nine epochs of folding and bathylithic formation accompanied by ore-deposition (see Table), and in addition a few epochs of hypabyssal intrusion and volcanic activity to which some ore-formation may be attributed.

#### *Pre-Cambrian.*

Probably for the world as a whole, as for Australia, the pre-Cambrian ores loom much larger than the sum total of all those of subsequent geological time. This may indicate, of course, that the pre-Cambrian was specially characterized by the introduction of ore-minerals, but it must be remembered that it embraced more than two-thirds of known geological time, and that it may have comprised several periods of deposition followed by epochs of folding and bathylithic injection, and punctuated by intervals of erosion sufficiently long to permit the complete elimination of all traces of the sediments. Professor Arthur Holmes has demonstrated by Pb/U determinations that at least seven distinct epochs of bathylithic injection and (presumably) orogenesis may be recognised for the pre-Cambrian. At present in the Commonwealth we have evidence of only three main periods of deposition and two main epochs of diastrophism and injection. The first or Pilbaran diastrophic epoch closed what we may call the Lower and the second or Houghtonian the Middle pre-Cambrian sedimentation. Probably the earliest metallogenetic epoch of which we have knowledge is that to which the gold ores of Kalgoorlie (W.A.) belong. There has been much controversy about the circumstances in which these ores were introduced, some workers relating them to the intrusions of the Younger Greenstones (dolerites) through their acid differentiates, a series of sodic porphyries and porphyrites, others preferring to connect them with hidden intrusions of granite similar to those occurring, with an accompaniment of auriferous quartz-veins, a few miles away. If the first view is correct, and it seems to have a good deal of justification, the epoch of metallization is probably Pilbaran, for the injection of the greenstones as sill-like masses seems to have heralded the Pilbaran folding, and indeed the rocks of the Younger Greenstone suite may be comagmatic with the granite-gneisses that were formed during the Pilbaran epoch. If on the other hand the gold is related to a granite, then its introduction most probably belongs to the Houghtonian epoch.

So far as we know, comparatively few ore-deposits are related to the Pilbaran intrusions. Apart from Kalgoorlie and a few other fields, such as Meekatharra and Wiluna, in which the gold ores are in greenstones and similar to those of Kalgoorlie, the only other known deposits which we can well assign to the Pilbaran epoch are the chromite contained in ultrabasic greenstones at Coobina in the north-west of Western Australia and the platinum which is present in rather insignificant amounts in certain altered basic or ultrabasic intrusions belonging to the Older Series in the Barrier Ranges near Broken Hill, New South Wales.

For Western Australia the Pilbaran and the Houghtonian were by far the most important epochs of ore-formation. During the second a great series of granitic bathyliths and stock-like masses were injected, with potassic and sodic pegmatites, and to them are related most of the gold occurrences of the State, together with a number of other ores, chiefly those of tin, iron, tungsten, molybdenum, tantalum and niobium, and minerals containing uranium, beryllium, lithium and the rare earths.

To the Houghtonian epoch also are assignable many ore-deposits outside Western Australia. In North Australia the gold of Buldiva, Pine Creek and a

number of other fields, the tin of Maranboy, the tantalum of Rum Jungle and the copper of Yeuralba all appear to be related to Houghtonian granites. Coming farther south we note that the gold of Tanami and The Granites and the auriferous hæmatite lenses of Tennant Creek are of the same age. At Hatches Creek are tungsten deposits, and in the Macdonnell Ranges the Oolgarra granites brought in the gold of the Winnecke, Arltunga and other fields, while the associated pegmatites have yielded beryl. Recently uranium has been reported from Hart's Range in the Eastern Macdonnells.

The chief primary ores of pre-Cambrian age in South Australia are the copper deposits of Wallaroo and Moonta, whose parent magma appears to have been that which produced the Houghtonian granites and pegmatites with which they are associated. A little uranium is associated with the copper ores. The uranium ores of Mt. Painter, in the extreme north of the Flinders Ranges, are in granitic igneous intrusions, but whether these are of Houghtonian age or later is still in dispute, as is likewise the age of the granites in the east of the State with which the radio-active ilmenite of Olary is associated. Traces of uranium minerals have also been noted in Houghtonian (?) pegmatites in Eyre Peninsula. Apart from rutile and monazite which are found in titaniferous pegmatites in a few places, there do not appear to be any further pre-Cambrian ores of note in South Australia.

Across the border the great silver-lead-zinc deposit of Broken Hill, with copper, gold, cadmium and other minor constituents, is most reasonably regarded as comagmatic with Houghtonian granites like those of Mundi Mundi, and farther to the north in the Barrier Ranges are pegmatites with tinstone, wolfram and amblygonite. The other easterly projection of the Great Western Plateau contains the copper and iron deposits of the Cloncurry region including those of the Cloncurry district, Mt. Philp, Mt. Oxide and a number of other outlying fields, together with the silver-lead and copper lodes of Mt. Isa. All these appear to be related to the Cloncurry and Templeton River granites. Much farther north the silver-lead of Lawn Hill is probably in part of the same age but perhaps partly younger. Rutile, beryl, monazite and other rare minerals occur in pegmatites west of Mt. Isa, related to the Templeton River granite. East of Cloncurry the pre-Cambrian disappear under Mesozoic beds, to emerge in the Etheridge and other goldfields, where some of the gold at all events seems to be pre-Cambrian and probably Houghtonian.

The possibility that some of the gold, silver-lead and copper of Western Australia, and particularly of the Pilbara area, is related to contemporaneous lavas of Nullagine (Upper pre-Cambrian) age and basic dykes of latest pre-Cambrian has already been referred to. The presence of these ores may be regarded as marking a minor pre-Cambrian metallogenetic epoch in Western Australia.

### *Cambrian.*

Upper pre-Cambrian seems to have passed into Palæozoic time without any orogenic break, and sedimentation continued till the end of the Middle Cambrian epoch. Most of it occurred in the great Central Basin, which included the sites of the Mt. Lofty and Flinders Ranges in South Australia and extended east into New South Wales and Queensland, and south and south-east to Victoria and Tasmania. In the north it embraced much of Northern Territory (including the Macdonnell Ranges) and spread into East Kimberley. At this time also the Tasman geosyncline was probably initiated in eastern Australia. During the Tyennan epoch, shortly after the close of the Middle Cambrian, Upper pre-Cambrian and Cambrian rocks were folded together, and there was injection of granites, pegmatites and quartz-veins along the southern and eastern Mt. Lofty Ranges and to the south-east into the far west of Victoria. The intrusions

seem to have extended north to the north-east of the Macdonnell Ranges, and granite was injected into the Upper pre-Cambrian rocks in the far north-west of New South Wales, in the Koonenberry, Wertago and Nuntherungie Ranges and at Tibooburra. At the same time granites, granite-porphyrries and syenites invaded the Lower and Middle Cambrian and Upper pre-Cambrian rocks of northern and western Tasmania at Middlesex Plains, Mt. Darwin and elsewhere.

These irruptions of magma were responsible for a limited amount of ore-deposition. They probably brought in the copper of the Mt. Lofty and Flinders Ranges fields, as at Burra, Kapunda, Balhannah, Callington, Blinman and Yudnamutana, and the gold of Mt. Grainger and other goldfields. The copper, however, may in part have come in with minor basic intrusions that intersect the Cambrian and Upper pre-Cambrian rocks. It has been argued that the magmas responsible for the radio-active ores of Mt. Painter and Olary invaded Upper pre-Cambrian rocks, and if so they are probably Tyennan. Some beryl-bearing pegmatites in the eastern Mt. Lofty Ranges may be of the same age, and so may the tungsten of Wauchope Creek in Central Australia.

In the far north-west of New South Wales the granites introduced copper and gold, and it may be that some of the Lawn Hill silver-lead ores of North Queensland, which are in gently folded Cambrian rocks, were emplaced during the same epoch.

Mineralization related to the Tyennan granites of Tasmania was not important or extensive; in fact only some copper and the iron-ores of the Jukes-Darwin field have been referred, and with some doubt, to their entry. If, however, as has been suggested, the ultrabasic intrusions of western Tasmania are Cambrian, then chromium, nickel and osmiridium minerals are to be added to the Tyennan ores.

On the whole this metallogenetic epoch was far from spectacular, except in South Australia, where more copper has been mined than in any other State.

#### *Ordovician.*

After the Cambrian period by far the most important metallogenetic events in the geological history of the Commonwealth occurred in eastern Australia, which was the site of the Tasman geosyncline. At the close of the Ordovician sedimentation came the Benambran epoch of folding and formation of synchronous bathyliths of somewhat acid granites with pegmatites. Diastrophism affected a broad median zone running through eastern Victoria and the highlands and Western Slopes of New South Wales, which must have been prolonged into Queensland. Two chief belts of granitic bathyliths are known, the more westerly of which, about 100 miles wide, starts in the highlands of eastern Victoria, passes through Albury and the Upper Murray country, to the east of Wagga, and north through Junee as far at least as a point 20 miles west of Condobolin. Some gold and tin in Victoria and in south-eastern New South Wales seems to have been introduced with the granite and pegmatites, and gold further north at Junee Reefs and Sebastopol, but this region was subjected to at least three subsequent epochs of folding and plutonic invasion, and it is by no means easy to determine beyond doubt the respective ages of all the ore-deposits. It is possible that some of the tin-ores of the Western Slopes, as at Mt. Tallebung, Buddigower and elsewhere, are Ordovician, but information on the point is lacking.

#### *Silurian.*

At the end of the Silurian Period during the Bowning epoch the geosyncline suffered further diastrophism except for a narrow zone in the extreme west. Synchronous bathyliths and porphyry lenses associated with the folding are widespread in the Eastern Highlands and Western Slopes of New South Wales

and extend into eastern Victoria. We find them in New England east of Armidale and south as far as Walcha, in the Central Highlands at Cow Flat and elsewhere south of Bathurst, at Crookwell and Wheeo north of Goulburn and probably also as far west as Nymagee. They are also seen at Breadalbane and Gunning, east and west of Lake George, about Adelong and Batlow, near Grenfell, in the Australian Capital Territory and south to Cooma, on the Kosciusko plateau, near Delegate, north of Albury and across the border into Victoria to the Omeo district. Many of the rocks are hybridized and of the composition of quartz-diorites. Gold seems to be genetically related to many of the gneissic granites and porphyries in Victoria and in New South Wales, as at Adelong, Cooma, Michelago, Tuena, Wyalong and perhaps too at Hillgrove (New England). Copper is known from Cow Flat, iron ore occurs at Breadalbane west of Goulburn, and a series of small deposits of iron and copper ores borders the Murrumbidgee batholith on its eastern side from the Cotter junction south to Cooma.

To the Bowning epoch are usually assigned the sheets of ultrabasic intrusives and serpentinized peridotites, pyroxenites, etc., which form two long submeridional belts on the South-Western Slopes, one running through Gundagai and the other to the east of it. A certain amount of gold has been yielded by these intrusions, but it is very doubtful if they are more than host-rocks, though they may have been comagmatic with granites and porphyries which were the probable ore-carriers. Chromite has been got from the ultrabasic rocks at several places. The platiniferous serpentine of Fifield is also possibly late Silurian.

No ore-deposits of late Silurian age have been definitely recognised in Queensland, though it is by no means unlikely that such exist. They may, of course, be largely hidden beneath the sediments of the Great Australian Artesian Basin.

#### *Middle Devonian.*

Tasmania and central Victoria escaped the Bowning orogeny, and Silurian and Devonian rocks there were deformed together during the Tabberabberan orogeny that brought the Middle Devonian epoch to an end. The belt of folding must have continued north into New South Wales, where we find a number of plutonic masses intrusive into Silurian and overlain by Upper Devonian rocks, which seem to belong to this epoch. They are of granite and/or granodiorite, and of subsequent type, and apart from field-relations there is no certain way of distinguishing between them and the Carboniferous intrusions, which resemble them petrologically and whose region of intrusion overlapped theirs.

No intrusions of this age are certainly known in Queensland, though the belt of folding must have extended into that State. The gold-bearing granites of Charters Towers were thought by Jack to be overlain farther north by Upper Devonian beds, and if so the gold of this field and of Ravenswood and other adjoining fields may be Middle Devonian. In New South Wales Andrews recorded from east of Parkes a granite which must be Tabberabberan, and not improbably it or an allied intrusion was responsible for the mineralization of the Forbes-Parkes area, in which the auriferous solutions took advantage of shear-zones in the Silurian sediments and contemporaneous andesitic flows. It may be with a granite of the same age that the wolfram of Yeoval is connected. In the Cobar-Nymagee-Mt. Hope area there are massive granites and porphyries locally crushed, which are probably comagmatic, intrusive into Silurian and overlain by Upper Devonian beds and therefore Tabberabberan. Their magma is most likely to have been the vehicle for the gold, copper and other ores of the region.

A composite bathylith of granite and granodiorite with marginal quartz-porphyrries and quartz-porphyrtes stretches north for some 50 miles from Bungonia near Goulburn to Wombeyan and beyond. There is but little mineralization known to be connected with it, but the silver-lead ores of the old Carrington mine near Marulan may be related to it, and so may the complex ores of the Tolwong mine on the Shoalhaven River.

In the Yass-Burrinjuck area are granites and porphyrites intrusive into Silurian and Middle Devonian rocks, and they are perhaps to be regarded as Tabberabberan and are probably responsible for the small silver-lead and copper deposits of the area. The intrusions seem to be continued south to the Tumut River, Yarrangobilly, Lobb's Hole and the country at the head of the Goodradigbee River, where small deposits of copper and silver-lead are associated with them. Farther north the wolfram of Frogmore is in granite of possibly the same age. The great bathylith running from Kiandra past Adaminaby and through Berridale, the Kosciusko plateau and Dalgety into Victoria is most likely Tabberabberan though perhaps younger. Gold, copper and a little wolfram are found with it.

In eastern and central-eastern Victoria many of the big intrusions may be Tabberabberan, but they are not easily separable from those of Carboniferous age. The diorites, intrusive into Lower Devonian beds, which brought in the gold of the Diamond Creek, Queenstown and Warrandyte fields, north-east of Melbourne, are probably of this age, and so is the remarkable swarm of dykes of intermediate to basic composition which follows the strike of the Silurian and Lower Devonian (?) beds of the Walhalla synclinorium in eastern Victoria; these are clearly related to the folding of the beds, which is Tabberabberan. The auriferous quartz-veins so abundant both in the dykes and in the folded sediments are comagmatic with the dyke-rocks. The gold-bearing granodiorites and porphyrites of the Strathbogie Ranges also seem to be Middle Devonian. As for the massive granites and associated gold deposits among the Ordovician schists of the north-east, it is very hard to tell their age; some of them are possibly Tabberabberan, and the same may be said for the copper and silver-lead at Buchan and Mt. Deddick.

In western Tasmania a series of granodiorites, porphyries and porphyrites, massive but passing into schistose phases, invades strata as high as Silurian and Lower Devonian, and may provisionally be regarded as Middle Devonian. With them came the deposits of copper, zinc, lead, silver and antimony in the Mt. Lyell, Zeehan, Rosebery and other fields.

#### *Lower Carboniferous.*

The Devonian passed into the Carboniferous Period with no orogenic interruption, but during and at the end of the Lower Carboniferous came the important Kanimblan epoch of folding, intrusion and metallogenesis. The whole of the Tasman geosyncline was affected save for a belt on the east coast of Queensland and New South Wales, and Kanimblan intrusions appear at intervals from the tip of Cape York Peninsula to the most southerly point of Tasmania. They show much magmatic differentiation and include very acid granitic types. With them are associated the gold deposits of Cape York Peninsula, and possibly those in the Hodgkinson and Herberton fields, at Croydon and Mt. Emu, and some of those of the Etheridge field. The extensive massive granites of the Charters Towers, Ravenswood and other neighbouring goldfields may belong to this epoch, though, as suggested above, they may be older. With the acid granites are associated the tin, wolfram and molybdenum ores of the Herberton region, and in the Herberton and Chillagoe fields there are silver-lead and copper. The Clermont and Mt. Wyatt goldfields may also be Kanimblan. There is some regional overlap between the Kanimblan and late



Permian invasions, and of some intrusions therefore the age is not precisely known. Iron ores are found in the Chillagoe and Mackay-Rockhampton-Gladstone districts.

In New South Wales the chief plutonic masses known to be Kanimblan crop out in the Central Highlands and their western slopes, forming composite bathyliths intrusive into rocks as high as Upper Devonian, as about Hartley, Oberon, Bathurst, Orange, Cowra and the country to the south. Further north is the Wuuluman bathylith in the Wellington Goldfield. Deposits of gold and copper are known in various places, generally in a country-rock of Silurian sediments or lavas as at Lucknow near Orange, Burruga, Hill End, Oberon, Blayney, Lyndhurst and Wellington. To this epoch also belong the copper and iron deposits of Cadia and Carcoar. On the South Coast are the Yalwal and Moruya gold-bearing intrusions, and farther west the great bathylith that passes through Braidwood, the Araluen Valley, Pambula, Bega, Cathcart and south into Victoria; associated with it are ores of gold, molybdenite and bismuth. The complex Captain's Flat ore-bodies, though emplaced in Ordovician and Silurian rocks, seem to be related to a neighbouring intrusion of Kanimblan (?) granite. Other granites in the Southern Highlands and South-Western Slopes may be of the same age, such as those of Tumbarumba, Holbrook, Henty and Ardlethan; they have brought in gold, tin and tungsten.

In Victoria there are probably many Kanimblan intrusions right across the State from Gabo Island to the Grampians, chiefly granites and granodiorites. Here, for instance, are to be placed the southern prolongation of the Bega bathylith, the granites of Mt. Buffalo, Baw Baw, Warburton and Glenrowan, the granodiorites of the Dandenongs, Mt. Macedon, Harcourt and Pyalong, and the granites and porphyries of the Grampians. In the far south-east are the granites of Wilson's Promontory and Cape Woolamai.

To these intrusions are related, it would seem, by far the great majority of the gold ores in the Palæozoic rocks of western and central Victoria, like those of Stawell, Castlemaine, Ballarat, Bendigo and Maldon; in some of these fields the connexion of the ores with the plutonic rocks is obvious, in others it is presumed.

Certain of the massive granites in the north-east of the State in the Ordovician metamorphic belt are probably of Kanimblan age, and to them perhaps are referable some of the tin, tungsten and molybdenum ores of that area, extending north into New South Wales.

The Kanimblan intrusions may be traced across Bass Strait into Tasmania both east and west. Many are of acid granite, and to them are related chiefly deposits of tin, tungsten and molybdenum ores, as on King Island, in the north-east at Aberfoyle, Stanley's Creek and Blue Tier, at Middlesex, and in the west at Heemskirk, Stanley River and elsewhere. The iron ores of Blythe River are Kanimblan, and if the ultrabasic intrusions of the island are really comagmatic with the granites as has usually been assumed, and not Cambrian as has lately been suggested, then ores of osmiridium, chromium and nickel are to be added to the Kanimblan list.

By virtue of the extent in latitude and longitude of the region affected, and the abundance and variety of its ores, the Kanimblan was easily the most important of the Palæozoic metallogenetic epochs of eastern Australia.

### *Permian.*

The Tasman geosyncline was very considerably narrowed by the Kanimblan orogeny, and the locus of sedimentation was pushed over to the east in Upper Carboniferous and Permian times. Towards the end of the Permian Period the beds in its eastern part suffered folding and invasion by massive granites, which crop out at intervals from Townsville south nearly to the Lower Hunter Valley.



The chief rock-types closely resemble those of the Kanimbla intrusions, and the related ores show a similar variety. Among the deposits assigned to this Hunter-Bowen epoch in Queensland are those of the goldfields of Mt. Flora, Mt. Chalmers and Mt. Perry in the Great Syncline, the great Mt. Morgan gold-copper lode and the gold of Mt. Biggenden and of Gympie. This last is not in visible relation to any granite-mass, and has actually been doubtfully referred by some to a later epoch. Near Brisbane a small silver-lead deposit is associated with the Enoggera granite which, though surrounded by Brisbane Schists of Ordovician or Silurian age, is thought to be Permian. Near Warwick is another silver deposit at Silver Spur, and in the extreme south-east of the State at Stanthorpe is the northern end of a great composite bathylith or series of bathyliths which crosses the border into New South Wales and continues south through New England to Walcha and beyond. In northern New England the granites are intrusive into Permian and overlain by Jurassic beds. Outlying intrusions belonging to the series extend over to the coast at Kempsey, Valla and elsewhere. Rock types range from intermediate to ultra-acid, and the most prominent associated ores are those of tin, tungsten, molybdenum, antimony and bismuth, with gold, copper and silver-lead. The most southerly known ore-deposit belonging to this epoch is the stibnite of Antimony Hill on the Allyn River among gently folded Lower Carboniferous beds and many miles from any granite outcrop.

Believed to have been injected during the same epoch but earlier than the granites is a great series of ultrabasic intrusions, now largely serpentinized, the chief occurrences being in the Great Serpentine Belt bordering New England on the west. This contains ores of chromium and nickel, and at Crow Mt., Wood's Reef and elsewhere gold has been mined, though whether it is related directly to the serpentine or to the intrusive granites is not known. Similar rocks which may be of the same age are known in south-eastern Queensland as far north as Rockhampton and have yielded chromite and nickel and cobalt minerals.

#### *Jurassic.*

The important Cracow goldfield in Queensland is situated amid folded Permian strata, and the mineralization is most naturally attributable to the late Permian Auburn granite a few miles to the east. Lower Jurassic (?) andesites and sediments lie horizontally on the Permian, and in these Denmead has found quartz-veins resembling those which carry the gold. He suggests that mineralization was related to the effusion of the andesites.

#### *Cretaceous.*

For most of eastern Australia the Hunter-Bowen was the last metallogenetic epoch. In the Mesozoic Era the axis of the Tasman geosyncline lay well over what is now the Tasman Sea, but on its western margin marine Cretaceous sediments were laid down in a restricted coastal area in south-eastern Queensland, and during the Upper Cretaceous Maryburian epoch the Cretaceous and other Mesozoic beds were folded intensely near the coast and more gently farther inland. Certain small plutonic and hypabyssal intrusions, intermediate and acid, which cut Mesozoic beds, are referable to this epoch, and with them some mineralization is associated. They are considered to be responsible for the gold of North Arm and the antimony of the Neardie field, both in the Gympie district, and a little gold and lead at Somerset Dam (Mt. Brisbane) on the Stanley River. Here, too, may perhaps belong the mercury of Kilkivan, emplaced in part in Mesozoic rocks, and it may be that the Cracow gold should be referred to this epoch.

#### *Tertiary.*

Apart from the Narlarla silver-lead in West Kimberley, no primary ore-deposits of any magnitude are known to be related to Tertiary igneous rocks, intrusive or extrusive.

## ORE REGIONS, PROVINCES AND DISTRICTS.

During any given metallogenetic epoch there was in general a variety of ores introduced. These, however acquired, may be looked upon as an integral part of the magma, intrusive or extrusive, with which they are associated. For the igneous rocks petrological kindreds and petrographical provinces have been determined by the prominence of certain elements or certain minerals of a common age in the component rocks, and in a similar way it may be found possible to distinguish ore provinces and ore regions. As it appears to be understood in this country, the term "ore province" has a purely geographical connotation, the question of age being ignored, perhaps because of a tacit assumption that the same magma with the same ore-constituents persisted under a given region throughout long intervals of geological time. But for the igneous rocks it has been shown that the petrological character of extrusions and intrusions has changed from time to time, and it does seem possible that a similar state of affairs may obtain for ore-deposits. Combining the considerations of space and time we may define an ore region as a major area within which



Fig. 2.—Pre-Cambrian ore regions and provinces.

ore-deposition occurred during a particular metallogenetic epoch. In general there will be a big variety of ores in such a region, but these are often segregated, and it may be possible to recognize smaller areas, either parts of an ore region or independent entities, characterized by dominance or predominance of ores of one or more elements; these we may call ore provinces, and even smaller and more specialized areas may be recognizable which may constitute ore districts. Since ore-deposition may have recurred several times in any given area, there may be overlapping of ore regions, provinces or districts of different geological epochs, and only a very intensive field-study will serve to differentiate them.

In Western Australia it is hardly possible to separate the pre-Cambrian ore regions of Pilbaran and Houghtonian age, but in the second of these epochs a large part of the State helped to constitute a very large ore region characterized by a general dominance of gold, with copper and iron almost as widely though by no means so abundantly distributed (Fig. 2). Simpson showed that in a coastal belt about 250 miles wide from West Kimberley to Norseman and Esperance there is a province abounding in lithium, beryllium, lanthanum,

cerium, tantalum and tungsten minerals. Some of these characterize separate ore districts; for instance tin and tantalum are associated in the south at Greenbushes, in the centre at Poona and Coodardy, and in the north at Moolyella, Wodgina and elsewhere in the Pilbara goldfield.

The pre-Cambrian ore-regions extend into North Australia, where gold and tin-tantalum provinces can be recognized, and the gold distribution extends far south into Central Australia.

In South Australia and western New South Wales there are provinces rich respectively in titanium and silver-lead and zinc, and the Moonta-Wallaroo area is a copper province. The Cloncurry ore-province of western Queensland is essentially a copper one with local concentrations of silver-lead and iron.

The Tyennan intrusions of Upper Cambrian time established an important copper province in the Mt. Lofty and Flinders Ranges, with gold and subsidiary ores of bismuth, molybdenum and uranium, which are in part restricted to separate districts. A copper-gold province was also constituted in the far

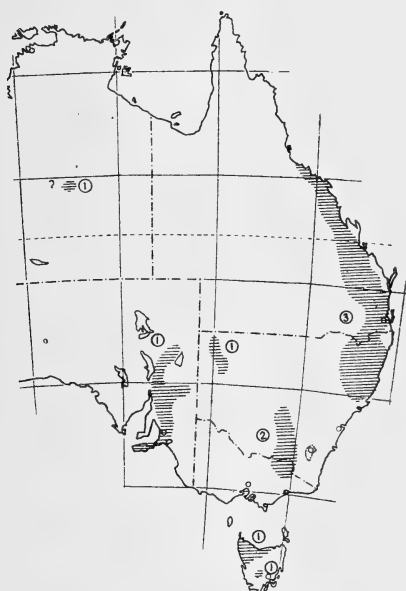


Fig. 3.—Upper Cambrian (1), Late Ordovician (2), and Late Permian (3) ore regions.

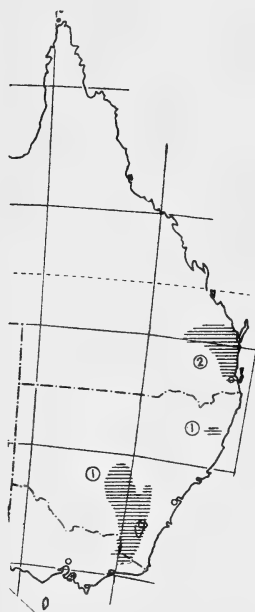


Fig. 4.—Late Silurian (1) and Late Cretaceous (2) ore regions.

north-west of New South Wales, and if the ultrabasic intrusions in the western half of Tasmania are of the same age, then this area also formed an Upper Cambrian ore-province with chromium, nickel and osmiridium (Fig. 3 (1)).

A late Ordovician (Benambran) gold-tin province seems to have been established in north-eastern Victoria and the adjoining parts of New South Wales, and may have extended in a north-north-westerly direction along the Western Slopes towards Condobolin (Fig. 3 (2)). The same general region may also have been a gold province in the late Silurian, and there were gold provinces and districts in the Central and Southern Highlands and on their western slopes as at Tuena, Adelong and Wyalong, also perhaps in New England. A long, narrow, iron-gold-copper province bordered the Murrumbidgee batholith on the east and a linear province was constituted by the chromite and nickel of Gundagai, Berthong, Wallendbeen and other centres (Fig. 4 (1)).

To the Tabberabberan ore region of New South Wales and Victoria belong the gold-copper deposits of the Cobar-Nymagee-Mt. Hope and the Forbes-Parkes provinces and the gold province of central-eastern Victoria from Queenstown and Warrandyte to Walhalla and Wood's Point. There was possibly a contemporary gold-copper province in western Tasmania and a gold province about Charters Towers (Queensland) (Fig. 5).

During the Kanimblan epoch eastern Australia contained a number of ore regions wherein several ore provinces and districts co-existed (Fig. 6). In the North Queensland region, for instance, which is broadly characterized by gold, there is the important Herberton-Chillagoe province with tin, silver-lead, copper, molybdenum and tungsten. To the same epoch may belong the Charters Towers (gold) and Clermont (copper-gold) provinces. The tin deposits of the country west of Cooktown mark a separate ore district. A linear iron province stretches along the coast between Mackay and the latitude of Maryborough.

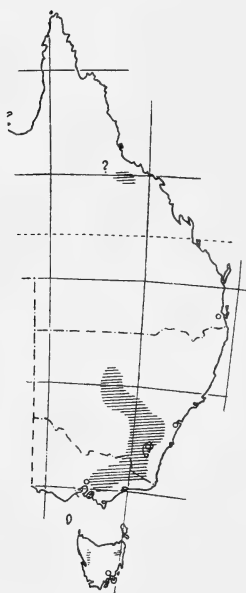


Fig. 5.—Late Middle Devonian ore regions and provinces.



Fig. 6.—Ore regions of late Lower Carboniferous time.

The southern region contains copper and gold widely distributed in the Central and Southern Highlands and Western Slopes of New South Wales, and a tin province in which the Ardlethan deposits are prominent. Small gold districts are seen at Yalwal and Moruya, and the Bega bathylith with its continuation into Victoria is marked by gold in the north and by molybdenum and bismuth farther south. The Victorian part of this region is essentially a great gold province in the western and central-eastern parts, with a few local concentrations of other metals, as of antimony at Heathcote and tin in the south-east.

At this time, too, an ore-province was formed in the northern half of Tasmania, wherein tinstone is the dominant economic mineral, with silver-lead, tungsten, bismuth and gold forming concentrations in various districts. This province is linked to Victoria through the King Island scheelite and the tin of Wilson's Promontory and, if the ultrabasic intrusions are Carboniferous and not Cambrian, by the osmiridium occurring at Waratah Bay.

# METAL

EPOCH	
Lower Pre-Cambrian (Pilbaran).	? Au of
Late Middle Pre-Cambrian (Houghtonian).	Au qua Ag at We in
Upper Cambrian (Tyennan)	(?) C ? A gol
Late Ordovician (Benambran).	
Late Silurian (Bowning) . .	
Late Middle Devonian (Tabberabberan).	
Late Lower Carboniferous (Kanimblan).	
Late Permian (Hunter-Bowen).	
Late Cretaceous (Maryborough).	



## TENTATIVE CORRELATIONS OF OROGENIC, INTRUSIVE AND METALLOGENETIC EPOCHS IN THE COMMONWEALTH OF AUSTRALIA.

EPOCH	WESTERN AUSTRALIA.	NORTHERN TERRITORY.	SOUTH AUSTRALIA.	TASMANIA.	VICTORIA.	NEW SOUTH WALES.	QUEENSLAND.
Lower Pre-Cambrian (Pilbarra).	? Au of Kalgoorlie, Wiluna, etc. ? Cr of Coobina in Ophthalmia Ra.	—	—	—	—	Pt. in Barrier Ra.	—
Late Middle Pre-Cambrian (Houghtonian).	Au associated with granite and quartz in most goldfields. Cu, Ag-Pb and Fe. Sn and Ta with Be at Greenbushes, Moolyella, Wodgina, etc. Rare carthos and U in pegmatites.	Au, Cu, Ag-Pb, etc., of Pine Ck. and Daly R. districts, Yeralba, Tanami, The Granites, Tennant Ck. and Arltunga and Winnecke fields. Sn at Maranboy, Buldiva, Yeralba, etc., and with Ta at Bynoe Harb., Rum Jungle and Finliss R. W, etc., at Pine Ck. and Hatches Ck. Be and U of Macdonnell Ras.	Cu, Au etc., of Wallaroo and Moonta, Tarcoola, Eyre Pen., Olary, etc. Ti, Be and Th in pegmatite at Normansville, Strathalbyn, etc. ? Some Au of Mt. Lofty Ras. U of Olary.	—	—	Ag-Pb, Zn and Cu of Broken Hill, Silverton, Thackaringa, Yanco Glen, etc. Sn, W and Li of Euriovie, Kattappa, etc.	Cu, Au, Ag-Pb, Zn and Fe, etc., of Cloncurry region, as at Cloncurry, Mt. Isa, Mt. Philip and Mt. Oxide. Au and Cu of Gilbert, Woolgar and Einasleigh fields. (?) Fe of Claude R. Ti, Ta and Be of Mica Ck. near Mt. Isa.
Upper Cambrian (Tyennan).	(?) Cu in valley of Ashburton R. ? Ag-Pb of Braeside in Pilbara goldfield.	Cu of Wollgorang-Redbank field. ? W of Wauchope Ck.	Cu, Au and Bi at Burra, Callington, Kapunda, Mt. Grainger, Blinman, Yudinmutana and elsewhere in Mt. Lofty and Flinders Ras. Ag-Pb of Glen Osmond, Callington, Strathalbyn, Kangaroo I., etc. ? U of Mt. Painter.	? Cu of Heazlewood and Fe of Jukes-Darwin field. ? Cr, Ni and Os associated with serpentine at Adamsfield and in the west and north-west (may be Kanimblan).	? Os at Waratah Bay.	Cu and Au at Werago, Koonenberry, Mt. Browne, Tiboburra, etc.	? Some Ag-Pb and Zn at Lawn Hill.
Late Ordovician (Benambra).	—	—	—	—	? Sn at Eskdale, Tallandoon and Mt. Walwa in the north-east, and ? Au at Bethanga, etc.	Au at Sebastopol and Junee Reefs. ? Sn at Holbrook, Balldale and Jingellie and perhaps at Mt. Talbung, etc.	—
Late Silurian (Bowning).	—	—	—	—	? Au in north-east at Granya.	Au at Adelong, Gundagai, Wyalong and at Trunkay, Tuena, Burrage and Rockley. Cu at Cow Flat. Au, Cu and Fe along east of Murrumbidgee batholith. Cr at Coolac, Gundagai, Berthing, etc. Pt. at Fifield.	—
Late Middle Devonian (Tabbernabarra).	—	—	—	(?) Cu, Au, etc., at Mt. Lyell, Jukes-Darwin, etc., on West Coast.	Au at Queenstown, Diamond Ck. and Warrandyte, N.E. of Melbourne. Au and Cu of Walhalla Wood's Point belt. ? Cu and Ag-Pb of Mt. Deddick and Buchan. ? Sn of Cudgewa Ck. in N.E.	Cu and Au in Cobarr-Canbelego, Mt. Hope, Nymagee, Tottenham and Condothin areas. Au at Forbes and Parkes. Cu and Ag-Pb in Yass-Burrowa district. ? Au at Kandra, Tumbarumba, Gundagai and Young. ? W at Yeoval, Frogmore and Berridale. Ag, Cu and Sn of Marulan and Tolwong.	? Au of Charters Towers, Cape R. and Ravenswood (may be Kanimblan).
Late Lower Carboniferous (Kanimblan).	—	—	—	Ag-Pb, Zn, Cu, Sn, W, Sb, Bi and Au of Zeehan, Read-Rosebery, Mt. Farrell, Dundas, Molina, Middlesex, Waratah and Stony Ck. and of the north-east. Fe of Blythe R. W of King I.	Au of Stawell and of the fields of the central-west, e.g. Bendigo, Ballarat, Daylesford, etc., also of Costerfield (with Sb). Some Sn in the N.E. and at Wilson's Promontory. W at Marysville and Warburton and Mo at Yen, Maldon, Mt. William, etc.	Au, Ag-Pb, Fe, etc., of Hill End, Orange, Bathurst, Blayney, Lyndhurst, and Wellington districts. Mo of Yetholme. Ag of Yerranderie. Au, Cu and Zn of Captain's Flat. Bi, Au and Mo of the Bega batholith. Au of Yalwal, Moruya, Araluen and Braidwood. ? Sn of Buddigower, Kikora, Ardethan and Pulletop.	Au of Claude R. and other fields in C. York Pen. and of Palmer R. and Mt. Wyatt. Sn, Ag-Pb, Cu, W, Mo, Bi, etc., of Chillagoe and Herberton districts, Star R., Cooktown, Silver Valley, Einasleigh, Cardross, etc. Au and Cu of Clermont. Au, Cu and Ag-Pb of Kilkivan. Au, W and Mo of Hodgkinson Field. Fe of Chillagoe and of Rockhampton-Gladstone belt.
Late Permian (Hunter-Bowen).	—	—	—	—	—	Au, Cu, Sn, Mo, W, As, Sb, etc., of New England and the North Coast, as at Drake, Kingsgate, Inverell, Hillgrove, Emmaville, Deepwater, Coramba, Valla, Cr, etc., of Great Serpentine Belt, New England and Port Macquarie.	Au and Cu of Mt. Morgan, Mt. Chalmers, Mt. Perry, Mt. Flora, Canoon, Cawarral, the Normanby, Eungella, Calliope, Gympie and other fields. Sn, W and Mo of Stanthorpe. Au and Ag-Pb of Enoggera. Ag of Silver Spur. ? Au of Cracow in part. Au, Fe and Bi of Biggenden. Cr, Ni and Co in serpentine at Pine Mt. and Kilkivan and in Rockhampton district.
Late Cretaceous (Maryborough).	—	—	—	—	—	—	Au at North Arm, Maronian and Yorkes. Au and Ag-Pb at Monsildale. Au and Ag at Mt. Brisbane. ? Some Au at Cracow. Cu and Pb in Maryborough area.

The ore region of the Hunter-Bowen epoch occupies a coastal belt in Queensland and New South Wales (Fig. 3 (3)). Gold and copper characterize a northern province including Mt. Flora, Mt. Morgan, Mt. Perry, Mt. Chalmers and Gympie, but farther south there are silver-lead ore districts at Enoggera and Silver Spur. The southern part, from Stanthorpe through New England and the North Coast of New South Wales, is best known as a province rich in tin, tungsten and molybdenum minerals, with smaller concentrations of bismuth, antimony and arsenic, and with districts, like that comprising Drake and Boorook, marked by gold and copper. A linear chromium-nickel province is determined by the serpentines bordering New England on the west.

The Maryburian ore region of south-eastern Queensland is very small, so far as it is at present known, and its deposits are of little economic importance (Fig. 4 (2)).

#### SUMMARY AND CONCLUSIONS.

In the table are summarized the metallogenetic epochs of the Commonwealth, chiefly those connected with plutonic intrusions, together with the principal ore-deposits that are thought to belong to them. Among the points revealed by the table one is the great importance of the pre-Cambrian epochs, to which are referred ore-deposits in all States of the Commonwealth except Victoria and Tasmania; another is the outstanding part played by the deposits of the Kanimblan and Hunter-Bowen epochs in eastern Australia. The gradual eastward migration of the loci of primary ore-deposition from Middle Palæozoic to the close of Mesozoic time is well shown, and it will be observed that the mineral wealth of States like Western Australia, South Australia and Tasmania is due to ore-introduction chiefly at two or at most three epochs, whereas in the east New South Wales had no less than eight metallogenetic epochs of varying importance. It would seem that in the matter of ore-introduction the synchronous granite bathyliths were of very much less significance than the subsequent.

The survey of the ore-regions, provinces and districts that I have given is obviously incomplete and in some respects tentative, but it does seem to be capable of expansion. An analysis of the ores in relation to the epochs of their introduction would draw attention to some curious features in the time- as well as the space-distribution of the ores. For instance, tantalum ores are confined, so far as we know, to the pre-Cambrian provinces of Western Australia, North Australia and Queensland, and uranium ores to the pre-Cambrian intrusions of Western Australia and Northern Territory and the pre-Cambrian and possibly Cambrian granites of South Australia. Osmiridium is found in quantity only in the ultrabasic Cambrian or Carboniferous province of Tasmania. Beryllium shows some preference for the granites of the pre-Cambrian shield and the Carboniferous and Permian intrusions of eastern Australia, and to judge from the known distribution of the detrital deposits the cerium, thorium and zirconium minerals were associated with pre-Cambrian granites in the shield and with Kanimblan and Hunter-Bowen intrusions in the east.

On the other hand, gold, copper, silver-lead and iron have been brought in in quantity by magmas of all geological ages, and ores of tin have an almost equally lengthy time-distribution.

What the significance of these things may be it is impossible to say in the present state of our knowledge, but they do suggest that the time-space conception of the distribution of ores may be of some importance.

Since I have been talking about ore-deposits it is perhaps appropriate that I should end on an economic note. In a recent address Dr. Raggatt, head of the Commonwealth Mineral Resources Survey, emphasized that our known



resources of ores were dwindling, and stressed the need for an intensive search for new deposits. If a detailed study could be made of the extent and boundaries of the known ore regions, provinces and districts, and of the nature of their contained ores, with due regard to the epochs as well as the places of ore-introduction, much time and energy might be saved by directing the search to the most favourable places. Such a study would be no doubt lengthy and laborious, but at all events the policy would be systematic and scientific, and I venture to suggest that in the long run it would be justified by results.

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## NITROGEN IN OIL SHALE AND SHALE OIL

### XI. NITRILES IN CRACKED SHALE GASOLINE.

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In an unsuccessful attempt to detect thiazoles in the tar bases isolated from cracked shale gasoline by reductive cleavage with sodium and alcohol, followed by the detection of a mercaptan (Morton, 1946), it was observed that an appreciable amount of ammonia was liberated. Since this ammonia was free from both primary and secondary amines, it was possible that it had been derived from the hydrolysis of some constituent of the bases rather than by the reduction. Nitriles are present to a small extent in crude shale oil (Mapstone, 1949), and it would also be possible that small amounts may be formed during the thermal cracking of the crude oil for the production of the gasoline (Mapstone, 1948). Traces of hydrogen cyanide have been found in the cracked shale gasoline (Mapstone, 1946) and it may be considered as the simplest nitrile—formonitrile. The work described here was therefore carried out to determine, if possible the, amount of nitriles present in the bases.

#### DETERMINATION OF AMMONIA FROM THE HYDROLYSIS.

Barta and Marschek's observation that pyridine and its homologues could be separated from ammonia by distillation from a citrate buffer at pH 3.0 (Barta and Marschek, 1937, 1938) was used as a basis for the determination of the amount of ammonia liberated during the hydrolysis. Two hundred millilitres of redistilled tar bases isolated from the acid sludge from the treatment of the gasoline (Mapstone, 1947) were hydrolysed by 50 ml. of 10% sodium hydroxide solution in a distillation flask fitted with a reflux condenser and inclined so that no condensate could collect in the side arm. Since ammonia has a much lower boiling point than the tar bases, it could be distilled off continuously as formed. However, with the very small quantity of ammonia involved it was necessary to reduce to a minimum the amount of the pyridine homologues that distilled with the ammonia, as well as to provide a carrier to transfer the ammonia from the condenser to the absorption solution. This was achieved by periodically purging the contents of the condenser into 100 ml. of sodium phosphate-citric acid buffer of pH 3.0 (Hodgman, 1940) by passing a stream of ammonia-free air through the side arm of the flask. By reducing the heating rate so that the level of refluxing vapours was just above the side arm at the time of purging, the amount of pyridine homologues carried over with the ammonia was kept between 5% and 30% of the amount of ammonia evolved.

When the hydrolysis was considered to be complete after one to one and a half hours, 10% to 20% of the buffer solution were distilled into 100 ml. of 1% boric acid, and the pyridine homologues that had been absorbed along with the ammonia determined by titration of the distillate with 0.1 N acid. The ammonia was then determined by rendering the remainder of the buffer solution strongly alkaline with 40% sodium hydroxide solution and distilling into a fresh boric acid solution.

## DETERMINATION OF ORGANIC ACIDS FROM THE HYDROLYSIS.

When cool, the dark brown layer of sodium hydroxide solution was separated from the tar bases, rendered strongly acidic with sulphuric acid, and distilled. The distillate was titrated with 0.1 N carbonate-free sodium hydroxide to a phenolphthalein end point for the determination of the organic acids. An appreciable amount of phenols was also present in the distillate.

The solutions containing the organic acids from all the analyses were bulked, acidified and distilled. The distillate was extracted with carbon tetrachloride to remove the phenols, neutralized with barium hydroxide, and evaporated to dryness. The dry barium salts were refluxed with ethyl alcohol and concentrated sulphuric acid; the sweet odour of the ester thus formed confirmed that the acids were organic. Three of five opinions were definite that the ester smelt like pineapple (ethyl valerate), and would therefore suggest that there was some valeronitrile (b.p. 141° C.) present in the bases.

## DISCUSSION OF RESULTS.

Two samples of the bases were examined: one which had been isolated about four years previously, and another which was freshly isolated for this work. In each case the analysis was carried out in duplicate. The agreement between the amounts of ammonia and organic acids obtained (Table 1) indicates that they were liberated in equivalent quantities during the hydrolysis, and that their precursors were most probably nitriles.

The small amount of nitriles thus found to be present in the tar bases is equivalent to approximately 0.05% by volume (calculated as valeronitrile). Since the bases are present to an extent of only 0.3% by volume in the cracked shale gasoline, the nitriles found are equivalent to approximately 1.5 p.p.m. in the gasoline. In connection with some other work, it was found that a single wash with 10% of concentrated sulphuric acid completely extracted 0.5% of benzyl cyanide from crude shale oil, so it is probable that the whole of the nitriles in the cracked shale gasoline were concentrated in the sludge from which they would be isolated along with the tar bases. The actual nitrile content of the untreated gasoline would no doubt be somewhat higher than the 1.5 p.p.m. found here as portion will probably have been hydrolysed by the caustic washes given the gasoline prior to acid treatment, and during the recovery of the bases from the acid sludge.

TABLE 1.  
*Hydrolysis of Bases.*  
(Results as milliequivalents per litre of bases.)

Bases.	Ammonia.	Organic Acids.
Old .. .. .	6.0	7.1
Old .. .. .	3.9	2.7
Old average .. .. .	5.0	4.9
Fresh .. .. .	5.1	7.9
Fresh .. .. .	6.9	5.7
Fresh average .. .. .	6.0	6.8

## SUMMARY.

The amounts of ammonia and organic acids obtained by the hydrolysis of the tar bases isolated from the acid sludge from the treatment of the gasoline indicate the presence of about 1.5 p.p.m. of nitriles in the original gasoline.

## ACKNOWLEDGEMENTS.

The author wishes to acknowledge the assistance of B. B. Mellor and K. Davidson in carrying out this work, and the permission granted by the management of National Oil Pty. Ltd., for the publication of this paper.

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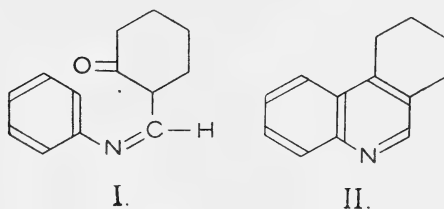
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# THE CYCLIZATION OF ANILS OF $\beta$ -KETO-ALDEHYDES.

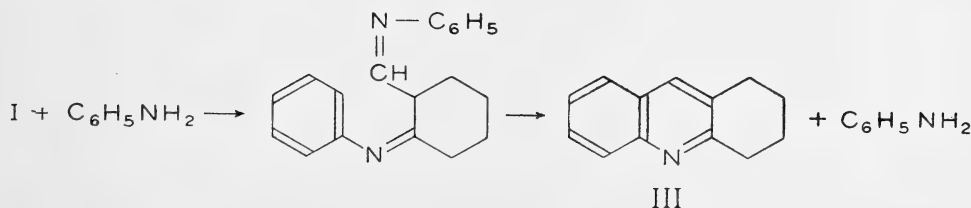
By G. E. CALF  
and E. RITCHIE, M.Sc.

*Manuscript received, May 23, 1949. Read, August 3, 1949.*

It is well known that anils of  $\beta$ -diketones are readily cyclized by acidic reagents to 2:4-disubstituted quinolines (e.g. Combes, 1888; Roberts and Turner, 1927). It would therefore be expected that anils of  $\beta$ -keto-aldehydes would form 4-substituted quinolines, but so far attempts to effect such cyclizations have been unsuccessful (Claisen and Fischer, 1888; Thielpape, 1922) or have given very low yields (Romet, 1935). Borsche (1910) also failed to convert 1-(phenyliminomethyl)-cyclohexan-2-one (I) to the tetrahydrophenanthridine (II) by heating it with concentrated sulphuric acid at  $100^\circ$ , obtaining only the *p*-sulphonic acid of I and a similar result was obtained from the *m*-hydroxy derivative of I. However, since the successful cyclization of I would lead to an attractive phenanthridine synthesis, we have studied this reaction more fully.

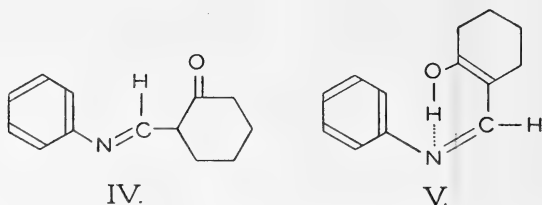


Numerous experiments were carried out in which I was treated with sulphuric acid of various concentrations at temperatures between  $0^\circ$  and  $100^\circ$ , but in each case it was either recovered unchanged or was sulphonated, and similar results were obtained with the methyl- and methoxy-derivatives of I. However, it was found that if these anils were refluxed with phosphorus oxychloride they were converted in 20–25% yield to bases which were identified as derivatives of 1:2:3:4-tetrahydroacridine (III). The same substances were formed, but in somewhat lower yields, by heating the anils with phosphorus pentoxide at  $250^\circ$  for a short time. The formation of these substances is best explained by the equations



which were originally suggested by Petrow (1942) to account for the formation of III when I was heated with aniline hydrochloride and zinc chloride in alcoholic solution.

The failure of anils of  $\beta$ -ketoaldehydes to cyclize normally has been explained by assuming that they exist in the *trans* configuration IV, which would be unfavourable to cyclization, rather than in the favourable *cis* configuration I. (Petrov, *loc. cit.*; Thielepape, *loc. cit.*)



However, no direct evidence for this assumption has been adduced and two strong objections may be made against it. Firstly, every analogy suggests that the anils are hydrogen bonded resonance hybrids, one of the chief contributing structures of which is shown by V, and which does have a configuration favourable to cyclization. Secondly, whatever the configuration of the anil itself may be, there is no reason to suppose that this configuration would be preserved in concentrated sulphuric acid (the usual cyclizing reagent). It appears then that some other explanation for the failure of anils of  $\beta$ -ketoaldehydes to cyclize smoothly must be sought.

#### EXPERIMENTAL.

The anils used in the following experiments were prepared by condensing *formyl*-cyclohexanone with aniline, *o*-toluidine, *m*-toluidine, *p*-toluidine, *o*-anisidine and *p*-anisidine respectively, in alcoholic solution (Petrov, *loc. cit.*).

##### *Cyclization by Phosphorus Oxychloride.*

The anil (10 g.) was gently refluxed with phosphorus oxychloride (30 c.c.) with exclusion of moisture for one hour. After cooling, the reaction mixture was poured into ice and water with vigorous stirring and when reaction ceased, filtered from resinous products. The filtrate was basified, extracted with ether and the product eventually isolated by distillation under reduced pressure in 20–25% yield. Final purification was effected by recrystallization from light petroleum.

##### *Cyclization by Phosphorus Pentoxide.*

An intimate mixture of the anil (10 g.) and phosphorus pentoxide (30 g.) was immersed in an oil bath maintained at 250° for fifteen minutes. After cooling, the reaction mixture was worked up as above, giving the tetrahydroacridine in about 10% yield.

The following tetrahydro-acridines, which were identified by their melting points, analyses (not quoted) and the melting points and analyses of their picrates (not quoted) were prepared by both of these methods: tetrahydroacridine m.pt. 56° (55°–56°), picrate m.pt. 220° (222°); 9-methyltetrahydroacridine, m.pt. 77° (77°–78°), picrate m.pt. 215°–216° (215°–216°); 8-methyltetrahydroacridine, m.pt. 100° (100°–101°), picrate m.pt. 186° (189°–190°); 7-methyltetrahydroacridine, m.pt. 62° (61°–62°), picrate m.pt. 189° (189·5°–190·5°); 9-methoxytetrahydroacridine, m.pt. 122° (121·5°–122·5°), picrate m.pt. 204° (206·5°–207·5°), and 7-methoxytetrahydroacridine, m.pt. 90° (90°–91°), picrate m.pt. 222° (223·5°–224·5°). The values given in brackets are those found by Petrov (*loc. cit.*).

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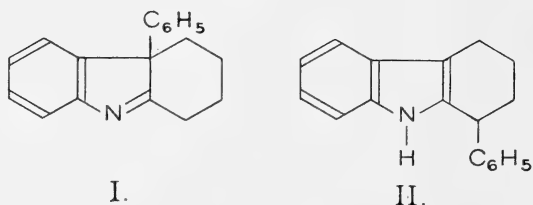
## SOME REACTIONS OF AN ANGULAR PHENYL COMPOUND.

By K. H. B. GREEN and E. RITCHIE.

*Manuscript received, May 23, 1949. Read, August 3, 1949*

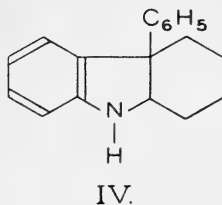
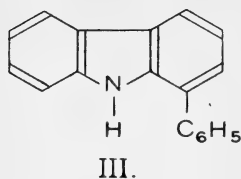
Substances containing an angular methyl group are well known from both natural and synthetic sources, but angular phenyl compounds are scarcely known. Allen and van Allan (1942, 1945) showed that when dimethyl-anhydroacetonebenzil was treated with acidic dehydrating agents it formed a bimolecular product containing an angular phenyl group. Allen, Bell, Clark and Jones (1944) prepared some naphthoquinone derivatives bearing angular phenyl groups and Boekelheide (1947) synthesized 9-phenyl decalin and 10-phenyl decahydroquinoline. However, very little is known of the reactions of such substances and since a characteristic reaction of the angular methyl group is its elimination on dehydrogenation, it was of interest to study the dehydrogenation and other reactions of an angular phenyl substance. The substance chosen was the readily accessible 11-phenyl-1:2:3:4-tetrahydrocarbazolenine.

When the oily phenylhydrazone of 2-phenyl *cyclohexanone* was refluxed with glacial acetic acid a vigorous reaction occurred and 11-phenyl-1:2:3:4-tetrahydrocarbazolenine (I) was formed in good yield together with a smaller amount of 1-phenyl-1:2:3:4-tetrahydrocarbazole (II). These substances are readily separated and distinguished from one another because I is basic and II is neutral. They were characterized by their yellow and reddish brown *picrates* respectively.

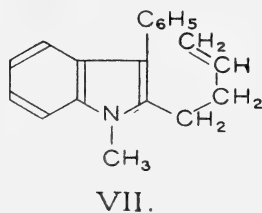
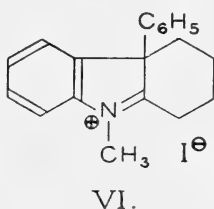
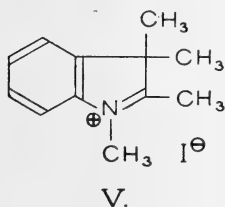


Barclay and Campbell (1945) have shown that tetrahydrocarbazoles, and hexahydrocarbazoles especially, are smoothly dehydrogenated by chloranil to carbazoles. When their procedure was applied to II it readily yielded 1-phenyl-carbazole (III), but I which might be expected to split off benzene and hydrogen yielded only uncrystallizable tars under a variety of conditions. Similarly the dehydrogenation method of Perkin and Plant (1923), i.e. refluxing with sulphur in quinoline, gave only black resinous materials. Since hexahydrocarbazoles are much more readily dehydrogenated than tetrahydrocarbazoles, I was reduced by tin and hydrochloric acid to 11-phenyl-1:2:3:4:10:11-hexahydrocarbazole (IV) and its dehydrogenation by these methods attempted. But again only tars were formed.

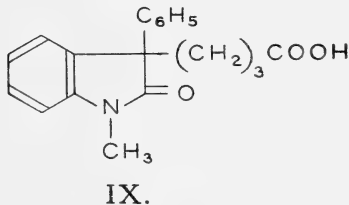
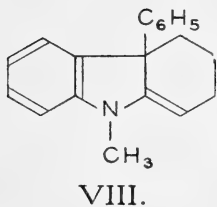




It has been shown (Ciamician, 1894) that when 2 : 3 : 3-trimethyl-indolenine-methiodide (V) is heated, it loses methyl iodide to form 1 : 2 : 3-trimethyl-indole. The similarly constituted *11-phenyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine-methiodide* (VI) however did not split off iodobenzene on heating, but instead gave a neutral substance,  $C_{19}H_{19}N$ , evidently formed by rupture of the reduced ring. It is probably *1-methyl-2-( $\Delta$ -3'-butenyl)-3-phenyl-indole* (VII).



A few other experiments also were carried out on VI. When treated with sodium hydroxide it yielded a base which although rapidly turning purple on exposure to air could be distilled under reduced pressure. Treatment of the distilled base with hydriodic acid regenerated VI and by analogy with the behaviour of V with alkali (Brunner, 1900) it is formulated as *9-methyl-11-phenyl-2 : 3 : 4 : 11-tetrahydrocarbazole* (VIII). Support for this structure was found in the observation that oxidation by permanganate produced an acid,  $C_{19}H_{19}NO_3$ , which must be *1-methyl-3-phenyl-3-(3'-carboxypropyl)-oxindole* (IX)-



#### EXPERIMENTAL.

*11-Phenyl-1 : 2 : 3 : 4-Tetrahydrocarbazolenine* (I) and *1-Phenyl-1 : 2 : 3 : 4-Tetrahydrocarbazole* (II).

When phenylhydrazine (12.8 g.) and 2-phenyl cyclohexanone (20.8 g.) were warmed together on the water bath, water soon began to separate. After 20 minutes the mixture was cooled extracted with ether, the solution dried and the ether removed. The residual thick oil, which, could not be crystallized, was cyclized by refluxing it in glacial acetic acid (150 c.c.) for one hour. After diluting with water, the reaction mixture was basified and extracted with ether. The ether solution was then extracted with dilute hydrochloric acid, washed and dried.

The acid extract on basification yielded the carbazolenine (I) which after crystallization from aqueous alcohol formed colourless needles (14.5 g.) melting at 128°.

Found : C, 86.5 ; H, 7.0 ; N, 5.7%. Calculated for  $C_{18}H_{17}N$  : C, 87.5 ; H, 6.9 ; N, 5.7%.

The *picrate* crystallized from alcohol in yellow rhombs melting with decomposition at 185°.

Found : N, 11.9%. Calculated for  $C_{24}H_{20}N_4O_7$  : N, 11.8%.

The ether solution on evaporation gave a thick gum which could not be crystallized. However, it readily yielded a crystalline *picrate*, which on decomposition furnished the tetrahydrocarbazole (II) which then crystallized from aqueous alcohol in large colourless needles (1.4 g.) which melted at 98°.

Found : C, 87.0 ; H, 6.8 ; N, 5.7%. Calculated for  $C_{18}H_{17}N$  : C, 87.5 ; H, 6.9 ; N, 5.7%.

Its *picrate* crystallized from alcohol in dark brown needles melting at 131°.

Found : N, 11.8%. Calculated for  $C_{24}H_{20}N_4O_7$  : N, 11.8%.

### 1-Phenylcarbazole (III).

A solution of chloranil (2 g.) and the tetrahydrocarbazole (II ; 1 g.) in pure dry xylene (30 c.c.) was refluxed for 24 hours. After cooling, the tetrachloroquinol was filtered off and the filtrate washed with aqueous sodium hydroxide, dried and evaporated under reduced pressure. The residue crystallized from alcohol in colourless plates (0.65 g.) melting at 139°.

Found : C, 88.4 ; H, 5.5 ; N, 5.7%. Calculated for  $C_{18}H_{13}N$  : C, 88.9 ; H, 5.4 ; N, 5.8%.

Its *picrate* separated from alcohol in magnificent red needles melting at 153°.

Found : N, 12.1%. Calculated for  $C_{24}H_{16}N_4O_7$  : N, 11.9%.

### 11-Phenyl-1 : 2 : 3 : 4 : 10 : 11-Hexahydrocarbazole (IV).

The carbazolenine (I ; 5 g.), concentrated hydrochloric acid (10 c.c.), alcohol (10 c.c.) and tin (10 g.) were refluxed on the water bath for six hours. Whilst still hot, the supernatant liquid was decanted from undissolved tin into a large excess of dilute sodium hydroxide. The product, isolated by extraction with ether, was finally crystallized from aqueous alcohol separating as colourless needles (2 g.) melting at 118°.

Found : N, 5.6%. Calculated for  $C_{18}H_{19}N$  : N, 5.6%.

Its *picrate* crystallized from alcohol in yellow needles melting at 175°.

Found : N, 11.8%. Calculated for  $C_{24}H_{22}N_4O_7$  : N, 11.7%.

### Methiodide of I.

When a solution of the base (I ; 5 g.) in methyl-iodide (15 g.) was allowed to stand at room temperature the product (VI) gradually separated. After three hours it was collected, washed with dry ether and recrystallized from aqueous alcohol separating as pale yellow prisms (6 g.) which on heating began to decompose at about 130°.

Found : N, 3.3%. Calculated for  $C_{19}H_{20}IN$  : N, 3.6%.

### Pyrolysis of VI.

The methiodide (VI ; 5 g.) was gently heated with a free flame at 30 m.m. until decomposition began and the pressure rose rapidly. After the reaction had subsided, and the pressure had fallen, a light amber viscous oil was distilled over. Its solution in alcohol gradually deposited VII (1 g.) which was finally obtained as slightly yellow needles melting at 107°.

Found : C, 86.7 ; H, 7.2 ; N, 5.7%. Calculated for  $C_{18}H_{13}N$  : C, 87.4 ; H, 7.3 ; N, 5.4%.

Its *picrate* crystallized from alcohol in fine brown needles melting at 99°.

Found : N, 11.8%. Calculated for  $C_{25}H_{22}N_4O_7$  : N, 11.4%.

### Action of Sodium Hydroxide on VI.

A solution of VI (5 g.) in hot water (200 c.c.) was treated with sodium hydroxide (10 c.c. of 10%) and the mixture cooled. The product (VIII) isolated by ether, distilled at 215°/3 mm. in almost quantitative yield as a viscous colourless oil. It crystallized on rubbing with light petroleum, but since it rapidly became purple on exposure to air further purification and analysis were not attempted. When treated with hydriodic acid VI was regenerated.

Its *picrate* crystallized from alcohol in yellow needles melting at 150°.

Found : N, 11.7%. Calculated for  $C_{25}H_{22}N_4O_7$  : N, 11.4%.

*Oxidation of VIII.*

A solution of potassium permanganate (1.5 g.) in water (15 c.c.) was gradually added to a boiling solution of VIII (5 g.) in acetone (15 c.c.). Reaction was rapid and after a short time the manganese dioxide was filtered off, washed with water and the combined filtrates evaporated to a small bulk. Acidification then precipitated IX which crystallized from aqueous alcohol in colourless needles (2.1 g.) melting at 146°.

Found: N, 4.5%. Calculated for  $C_{19}H_{19}NO_3$ : N, 4.5%.

## ACKNOWLEDGEMENT.

The authors gratefully acknowledge their indebtedness to Miss J. Fildes, B.Sc., for the analyses which appear in this paper.

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# ANODIC AND CATHODIC POLARIZATION OF COPPER IN ACETIC ACID.

By R. C. L. BOSWORTH, Ph.D., D.Sc.

With five figures.

*Manuscript received, July 13, 1949. Read, September 7, 1949.*

## INTRODUCTION.

In a series of papers the author (Bosworth, 1949) has described an attempt to apply the principles of dimensional analysis to metallic corrosion. From studies of the rates of corrosion under standardized conditions of forced and natural convection it was found that five properties were concerned in determining the rate of corrosion for a given system under given external conditions. These properties were :

- (a) A maximum corrosion rate ( $q_0$ ) given by the rate at which corrosion would proceed were all limitations due to slow diffusion or convection made negligibly small.
- (b) A conductivity term ( $j$ ) equal to the rate at which the liquid acting as the corrodant would allow the controlling depolarizing agent to flow to the surface under unit driving force or potential difference for the type of flow concerned.
- (c) A capacity term ( $K$ ), or the change in the driving force for unit change in the concentration of the depolarizing agent produced by means of the corrosion reaction.
- (d) The density change produced by unit change in the concentration of the depolarizing agent, and
- (e) The driving force ( $E$ ) for the corrosion reaction.

However, the experiments already described were capable of giving only four independent properties. They gave no measure of  $E$  and further gave only  $j$  and  $K$  figures in terms of the products  $jE$  and  $KE$  respectively. It thus appears desirable that some method of estimating  $E$  for the systems considered earlier be investigated.

The quantity  $E$ , if it is to be a measure of the potential for the flow of the depolarizing agent from bulk of the corrodant liquid to the metal surface, must clearly be some measure of the work done in taking unit quantity of the agent from a combined state on the metal surface, and, completely undoing all associated chemical reactions at constant temperature and pressure, take it to a free state in the bulk of the corrodant liquid. If the flow is to be measured in terms of the movement of any essential reagent concerned in the corrosion reaction the associated potential could be measured in terms of the work done (multiplied if necessary by any convenient, but constant, factor) in allowing unit quantity of the reagent concerned to be taken from metal surface to bulk liquid by a reaction which undoes the process of corrosion. Since the flow has been recorded in terms of the passage of unit mass of metal from surface to liquid, the potential is obviously a measure of the work done to send unit mass of metal back again to the surface, and this is equal to the (non-molar) Gibbs' free energy

for the particular reaction concerned. A measurement of the e.m.f. which just balances the tendency of the metal to dissolve is, at constant temperature, a constant multiple of this quantity.

The effective e.m.f. given by an electrode placed in an electrolyte with which no approximately reversible chemical change is possible is (as pointed out by Gatty and Spooner, 1938, p. 23) the net effect of two possible exchanges between the metal and the electrolyte. In one the metal is behaving anodically and supplying positive ions to the solution, and in the other it is behaving cathodically and receiving positive ions from the solution. If the two reactions when balanced electrically, as they must be when the charge on the electrode has ceased to change, are not balanced chemically, then a net reaction must take place at the surface. This net chemical reaction can always be balanced against a net electrical potential obtained by making the anodic areas more negative and thus repressing the dissolution of metallic ions, and by making the cathodic areas more positive and thus repressing the deposition of hydrogen ions. Direct measurement of the external potential difference between the anodic and cathodic areas required to repress the reaction is not possible and an indirect method must be devised. The method adopted was that of measuring, as a function of the current, the p.d. between electrodes anodically and cathodically polarized and an unpolarized electrode to which no net current flowed and which therefore came to a potential with respect to the solution determined by electrical balance of the anodic and cathodic reactions. The polarizing current used is a measure of the rate of transfer of ions from the anodic to the cathodic areas, and the polarization is a measure of the internal resistance offered to this transfer. When the rate of transfer of ions is made electrochemically equivalent to the quantity  $q_0$  then the arithmetic sum of the overpotentials must be equal to the required driving force  $E$ . In this paper we will be concerned only with a measure of the driving force for copper in acetic acid-acetic anhydride mixtures. Other systems could be studied in a similar manner.

To convert our  $q_0$  values into the equivalent current density terms we require a knowledge of the valence of the copper ion actively concerned in the electrode reaction. Since experiments have shown that the rate of corrosion of copper in acetic acid is increased threefold or more by the addition of small amounts of cupric ions to the solution (for example by dissolving 1% of cupric acetate in the acetic acid), it is therefore reasonable to assume that the oxidation-reduction reaction



plays at least an important part in the anodic attack. On this basis we may write the current density ( $i$ ) in amperes per sq. cm. as electrochemically equivalent to a corrosion rate of

$$5.69 \times 10^6 i \text{ mgms. dm.}^{-2} \text{ day}^{-1}$$

So that if we find the sum of the two overpotentials when  $i$  is made equivalent to the recorded values of  $q_0$  we have a means of deducing the driving force, or corrosion cell e.m.f.'s  $E$ .

Quite apart from this use of the experimental data to give a quantity concerned in corrosion problems in acetic acid media, the general behaviour of polarized electrodes in non-aqueous solvents is a subject which is now receiving some attention, particularly at the hands of Bockris (1947) and his collaborators.

#### EXPERIMENTAL.

Since the complete curves of anodic and cathodic overpotential versus current density were required, and further since the electrolytes to be used were often of very low electrical conductivity, the commutator method was employed.

An outline of the circuit diagram is given in Figure 1. In this circuit a battery B drives a primary current through a milliammeter A, controlling resistance R, standard set of resistances (decade box) S, and triple gang commutator  $C_1$ ,  $C_2$ ,  $C_3$  to the triple electrode system  $E_1$ ,  $E_2$ ,  $E_3$ .  $E_1$  was the cathode,  $E_3$  the anode, and  $E_2$  a reference electrode. The milliammeter A was used only in setting a suitable value for the polarizing current. The value of the current was determined by measurement of the p.d. across S. During that commutator half cycle for which no primary current flowed in the electrode circuit the electrodes were connected to the triple throw, double pole switch T, the reference electrode and cathode to  $T_1$  and the anode and reference electrode to  $T_2$ . The third pole  $T_3$  of the switch was connected across the standard resistance S only during the half cycle for which primary current is flowing, for the other half of the cycle  $T_3$  was an open circuit. The switch terminals lead to a potentiometer which thus could measure the polarizing current (p.d. across S), the cathodic polarization (p.d. between  $E_2$  and  $E_1$ ) or the anodic polarization (p.d. between  $E_3$  and  $E_2$ ).

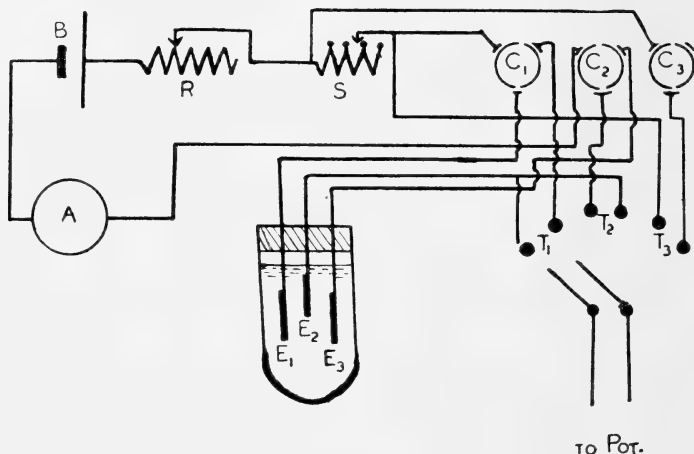


Fig. 1.

The electrodes were of copper strip 1.25 cm. wide and immersed 4 cm. in the electrolyte. The copper surfaces were prepared by polishing with gauge 0 emery paper followed by heating to dull redness and quenching in alcohol. The electrolytes used were 50% and 80% aqueous acetic, glacial acetic acid (95%) and acetic anhydride. In the former two electrolytes the battery B was a six-volt storage battery and in the latter two a two hundred-volt battery eliminator was used with suitable modification to the resistances.

The mechanical commutator method as here used has been regarded with suspicion when used with the more usual aqueous solutions on account of the decay of the polarization current during the "off" cycle of the commutator. Here where we are dealing with solutions of high electrolytic resistivity, low ionic concentration and high permittivity, it is to be expected that the time of discharge of the surface double layer will be large. Indeed the use of various commutator speeds from 40 to 400 r.p.m. have shown that the polarization curves in the liquid of lowest resistivity (the 50% acetic acid) are independent of the commutator speed over this range.

*The Polarization Curves.*

The experimental results for the current density versus anode and cathode polarizations are shown in Figure 2. The current density recorded is that for the charging half cycle only, and not the average value over the whole cycle as read by the milliammeter A. Several interesting features emerge from these graphs. In the non-aqueous solutions the anodic and cathodic polarizations are approximately equal at equal current densities ( $i$ ). The measured polarizations are not exactly the same as normal overvoltages which are measured against a reversible reference electrode, whereas the reference electrode in the present experiments is at a non-reversible corrosion potential. Nevertheless the measured polarization ( $V$ ) will differ only slightly in magnitude for normal anodic and cathodic overvoltages, and certainly the sum of the two polarizations will be equal to the sum of the anodic and cathodic overvoltages.

In all four cases of polarization in the non-aqueous solvents a plot of  $\log i$  versus  $\log V$  gave satisfactory straight lines. These lines are shown in Figure 3. From the slopes of these lines we may calculate factors  $\alpha$  defined as

$$\alpha = 2 \cdot 303 \frac{RT}{F} \frac{d \log i}{d \log V} \dots\dots\dots (1)$$

The factors  $\alpha$  and the quantities  $i_0$  (the antilogs of the intercepts) calculated from the curves shown in Fig. 3 are given in Table 1.

TABLE I.  
*Polarization of Copper at 27° C.*

Electrolyte Used.	Anodic Polarization.		Cathodic Polarization.	
	$i_0$ in amps. cms. <sup>-2</sup> .	$\alpha$	$i_0$ in amps. cms. <sup>-2</sup> .	$\alpha$
Glacial acetic acid ..	$7 \cdot 1 \times 10^{-7}$	0.184	$7 \cdot 6 \times 10^{-7}$	0.168
Acetic anhydride ..	$4 \cdot 5 \times 10^{-7}$	0.127	$4 \cdot 5 \times 10^{-7}$	0.102

Collected data on the two factors  $i_0$  and  $\alpha$  have been given by Bowden and Agar (1938). For cathodically polarized copper in aqueous mineral acids  $i_0$  ranges from  $10^{-5}$  to  $10^{-6}$  and  $\alpha$  from 0.8 to 0.5. Similar values of  $\alpha$  have been recorded for oxygen overvoltages (Bowden, 1929), while smaller values of the order 0.25 were recorded by Bowden and Kenyon (1935) for hydrogen overvoltages in alkali solutions. Since  $\alpha$  measures the rate of variation of the activation energy for deposition of ions with the external field, it has been concluded that the mechanism for deposition of hydrogen (cathodic overvoltage) is different in alkaline solution from that in (aqueous) acids. The figures recorded above for the non-aqueous conductors examined indicate still lower values for  $\alpha$  and thus still less dependence of the activation energy for the deposition of ions on the external field.

In the more nearly aqueous solutions the curves of Fig. 2 show an anodic polarization much less than the cathodic. In the 50% solution the cathodic polarization remains quite small until a current density of the order  $10^{-5}$  amp. cms.<sup>-2</sup> is reached when the polarization increases rapidly with further increase in the current density obtaining a maximum value of 0.74 volt and thereafter *decreasing* with further increase in the current density in such a way that the sum of the two polarizations remains constant and equal to 0.79 volt. The

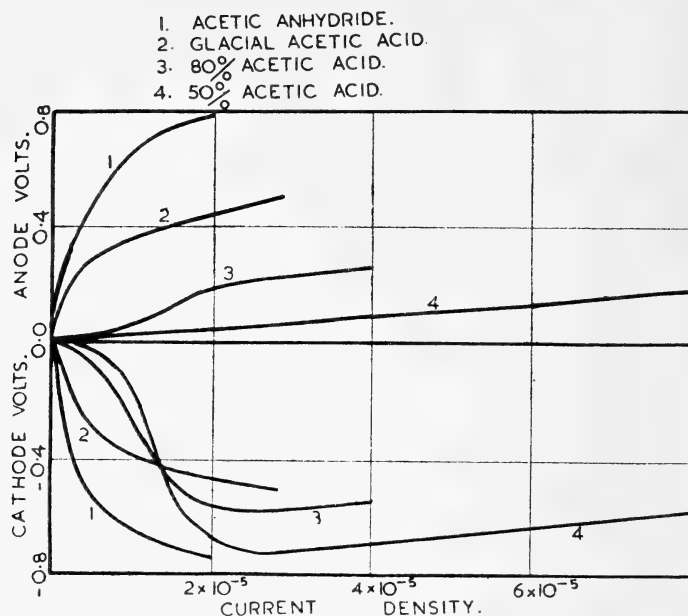


Fig. 2.

behaviour of the 80% solution is in a way intermediate between that of the 50% and the 95% solution, showing a less abrupt rise in the cathodic polarization and intermediate values for the anodic polarization. Detailed examination of the polarization curves show that neither of these solutions follow the exponential law

$$V = b(\log i - \log i_0)$$

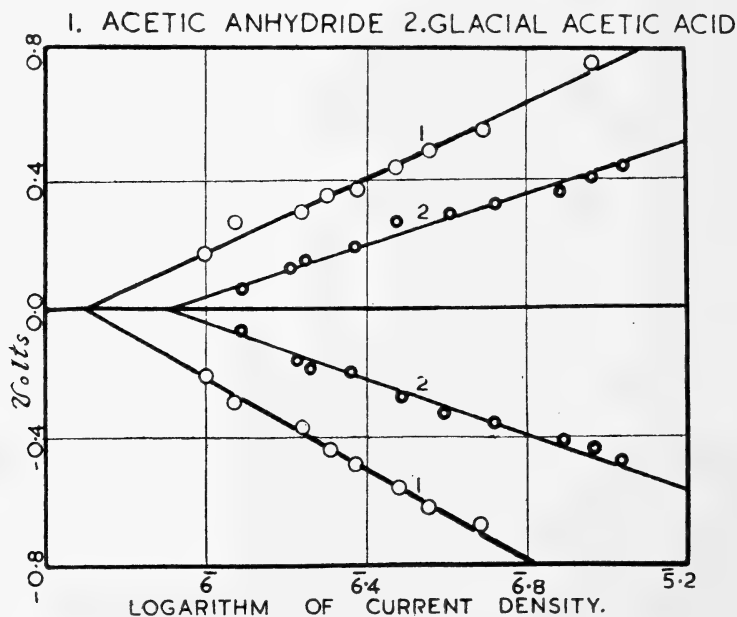


Fig. 3.



even approximately over any appreciable range. It is accordingly impossible to derive values of  $\alpha$  or  $i_0$  for these systems.

The data as given in Figure 2 refer to unstirred solutions initially saturated with air. Solutions prepared by boiling and cooling in a stream of hydrogen gave substantially the same curves. The act of stirring the electrolyte had but little effect on the anodic overpotential, but produced a very severe reduction of the cathodic overpotential in the region of current density in which the overpotential is rapidly rising. After a change in current density the overpotential generally settled down within a minute or two to the final new value. Again, however, in the case of the cathode in the region of rapidly changing overpotential the value at any fixed current density increased with time over a longer period and approached the final value only after about 20 minutes. The depression produced by stirring was again only of a temporary nature and the original value was restored on standing.

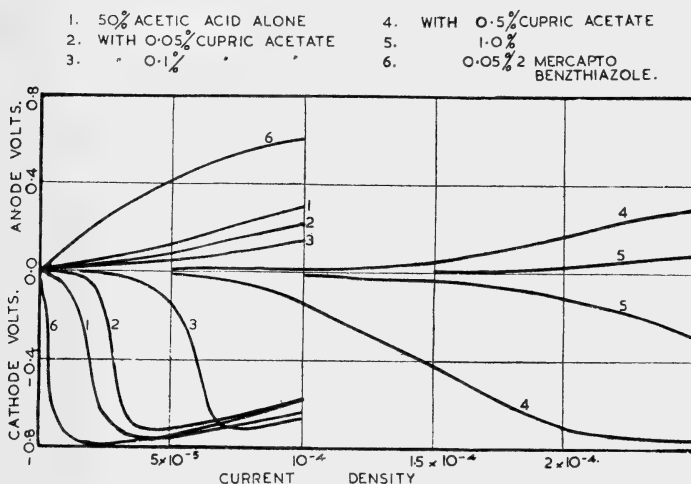


Fig. 4.

There was, however, a limit to which the effect of slow changes could be studied in these systems. On standing the copper electrodes slowly dissolved in the acetic acid, and since the presence of copper acetate in solution profoundly modified the nature of the polarization curves it was necessary to change the acid at fairly frequent intervals, particularly when dealing with high current densities. The effect of cupric ions on the polarization curves in 50% acetic acid is shown in Figure 4, where the polarization curves are given for systems with various quantities of cupric acetate added. At any fixed current density the addition of cupric acetate lowers both anodic and cathodic overpotential and also moves the point of rising cathodic overpotential into progressively higher and higher current densities. Cupric acetate is a corrosion accelerator in this system.

The opposite effect is shown by mercapto-benzthiazole, a corrosion inhibitor for copper. The addition of 0.05% of this substance both raises the overpotential and shifts the region of rapidly changing cathodic overpotential to lower current densities. A polarization curve for copper in 50% aqueous acetic acid with the addition of 0.05% of 2-mercaptobenzthiazole is also shown in Figure 4.

So far no chemical interpretation of the anodic and cathodic reactions concerned in the polarization observed in these liquids has been attempted. All the anodic polarization curves and the cathodic curves for glacial acetic acid and for acetic anhydride follow, as has already been indicated, a Tafel equation. However, the form of the cathodic polarization curves for the 50% and 80% aqueous acetic acid resembles that of a polarographic curve and strongly suggests that a change in the mechanism of the transport of the electrical charge occurs over a comparatively narrow range of current densities, the change involving the replacement of ions of comparatively low overvoltage by those of higher overvoltage as effective carriers to the cathode surface. Such a change, for example, might consist in the replacement of copper ions, originating from copper dissolved at the anode, by hydrogen ions when the current density becomes too heavy for transport by the attenuated array of copper ions. If this interpretation is correct a linear relationship is to be expected between the concentration of copper ions and the current density at which the change in the nature of the cathodic reaction occurs. Figure 5 shows the concentration of

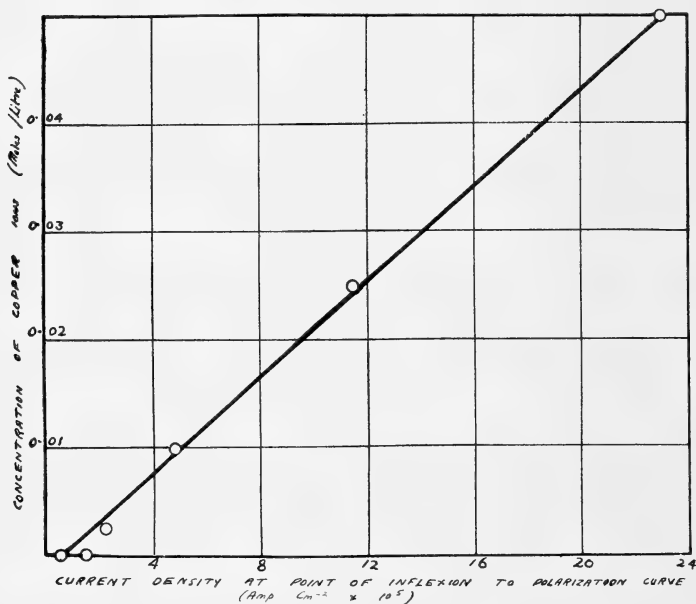


Fig. 5.

cupric ions  $\text{Cu}^{++}$  plotted against the current density  $i_{\text{crit}}$  required to give the point of inflexion on the cathodic polarization curve. The data used were those obtained from Figure 4. Figure 5 shows a linear relationship between  $\text{Cu}^{++}$  and  $i_{\text{crit}}$ . The extreme left-hand point on the figure refers to the solution of 2-mercaptobenzthiazole and an interpretation of the effect of this substance on the cathodic polarization curves now becomes clear. 2-Mercaptobenzthiazole forms a stable complex with cupric ions and thus reduces the current density which may be carried by these ions.

From the slope of the line shown in Figure 5 it will be seen that

$$\frac{d i_{\text{crit}}}{d \text{Cu}^{++}} = 4.5 \text{ amps. cms. moles}^{-1}.$$

Now it may readily be shown by solution of the Fick diffusion equation (see for example Kolthoff and Lingane, 1941, p. 435) that the limiting diffusion current is given by

$$\frac{d i_{\text{crit}}}{d C} = \frac{D}{\delta} z F,$$

where  $D$  is the diffusion coefficient for the ions deposited,

$\delta$  is the thickness of the diffusion layer at the electrode,

$z$  is the valence of the ions ( $z=2$  for cupric ions), and

$F$  is the Faraday.

The diffusion coefficient for copper ions in dilute aqueous solution is given (Kolthoff and Lingane, p. 45) as  $7.2 \times 10^{-6}$  cms.<sup>2</sup> secs.<sup>-1</sup>. It is not expected that the value would be very different in dilute solution in acetic acid. Frenkel (1946) has remarked on the striking constancy of the diffusion coefficients in different liquid solvents. Accordingly we may use the equation above to derive an approximate value for the effective diffusion layer thickness ( $\delta$ ), namely

$$\delta = 0.3 \text{ cm.}$$

which may be compared with the figure of 0.03 cm. quoted by Glasstone (1941) as a typical diffusion layer thickness for unstirred solutions at room temperatures. The deduction thus appears to lend considerable support to the suggestion that the lower part of the cathodic polarization curves is associated with the discharge of cupric ions.

The upper part of the polarization curves in these same solutions is presumably due to hydrogen deposition. Here also no equation of the Tafel form appears to be applicable. Indeed the measured overvoltage in all cases drops with further increase in the current density, suggesting, on taking the observations at their face value, that the hydrogen film formed at the higher current densities is electro-negative in character, similar, for example, to the hydrogen films formed on tungsten *in vacuo* (Bosworth, 1937).

However this apparent drop in the cathodic overvoltage may or may not be real. The commutator method of investigation used in this work is known to give low figures at high current densities (Ferguson, 1947). Use of the direct method of measurement in this work was excluded on account of the high resistivity of the liquids under test. In some cases the total p.d. between anode and cathode (net polarization plus ohmic drop in solution) was over 200 volts during the charging half of the commutator cycle, while the total measured polarization during the open half of the commutator cycle was less than one volt. The time constant for the decay of the overvoltage film is equal to the product of the resistance and the capacity, both measured per unit area of electrode surface. Bowden and Grew (1947) have found an electrostatic capacity (for a mercury-sulphuric acid interface) of  $20 \mu\text{F cm.}^{-2}$  and other workers have reported figures of a similar order of magnitude. As mentioned above, the resistivities of the liquids used in this work were abnormally high, ranging from 40,000 to 10,000,000 ohms per square centimetre of the electrode surface. It is thus to be expected that the time constants for the decay of the overvoltage films would be of the order 0.8 to 200 seconds. Since the commutator remained in the "open" condition for only 0.2 secs., it is not to be expected that errors due to rapid decay would be appreciable except, possibly, in the more highly conducting liquids (50% aqueous acetic acid with copper acetate in solution) and at the highest current densities, and it is only here that difficulties in the interpretation of the results were experienced.

*The Corrosion Cell E.M.F.'s.*

The corrosion cell e.m.f.'s for copper in these liquids may be derived from the curves shown in Figure 2. Data were first obtained for the rate of corrosion of copper specimens, from the same batch as the electrodes, at 27° C. and in acetic anhydride, acetic acid and 50% aqueous acetic acid. The test surfaces consisted of plane faces surrounded by a "guard ring" of the same metal, held horizontal and immersed at different depths ( $z$ ) below the free surface of the corrodant. The rate of dissolution  $q$  of the face (in milligrammes per square decimetre per day) was measured as a function of  $z$  and by extrapolation to zero  $z$  a corrosion rate  $q_0$  is found which is assumed to be the rate when there is no limitation of the chemical attack due to slowness of the diffusion to or from the surface. Details of these measurements have already been given (Bosworth, 1949). The values of  $q_0$  are then converted into equivalent current densities. The sum of the overvoltages at these current densities was then read off from Figure 2 and this sum was taken as a measure of the corrosion cell e.m.f. The results thus obtained are given in Table II. It will be noted in particular

TABLE II.  
*Maximum Corrosion Rates and Cell E.M.F.'s for Copper.*

Electrolyte.	$q_0$ .	Equivalent Current Density.	Cell E.M.F.
Acetic anhydride .. ..	51	$9.0 \times 10^{-6}$ amps. cms. <sup>-2</sup>	1.30 volts
Glacial acetic acid .. ..	100	$17.7 \times 10^{-6}$ " "	1.00 "
50% acetic acid .. ..	97	$17.1 \times 10^{-6}$ " "	0.70 "

that the value for  $q_0$  in 50% acetic acid is beyond the inflexion of the cathodic polarization curve. This must clearly be so as the deposition of cupric ions cannot be the cathodic reaction in the corrosion of copper.

## SUMMARY.

The cathodic and anodic overpotentials of copper in 50% and 80% aqueous acetic acid, in glacial acetic acid and in acetic anhydride have been measured as a function of the current density by the commutator method, it having been shown that the time constants in these poorly conducting media are long.

The two non-aqueous liquids gave polarization curves of the logarithmic type. The dimensionless factors  $\propto \left( 2.303 \frac{RT}{F} \frac{d \log i}{dV} \right)$  calculated from the slopes

are only of the order 0.10 to 0.18, the anodic value being slightly lower than the cathodic. These low figures indicate that the activation energy for the deposition of ions in these solvents are much less effected by external fields than in aqueous solutions.

In 50% aqueous acetic acid the cathodic overpotential shows a sudden rise over a narrow range of current densities. The current density at which this rise occurs is directly proportional to the concentration of cupric ions present in the acetic acid solution. The addition of 2-mercaptobenzthiazole which lowers the concentration of free cupric ions produces a high cathodic polarization at very low current densities and incidentally is a very effective corrosion inhibitor.

Corrosion cell e.m.f.'s have been deduced from a combination of the over-voltage curves with independently measured corrosion rates. These e.m.f.'s

are : 1.3 volts, copper in acetic anhydride ; 1.0 volts, copper in glacial acetic acid ; and 0.7 volt, copper in 50% aqueous acetic acid.

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## THE CHEMISTRY OF RUTHENIUM.

### PART III. THE REDOX POTENTIALS OF THE RUTHENIUM II COMPLEXES WITH SUBSTITUTED DERIVATIVES OF 2:2' DIPYRIDYL AND O-PHENANTHROLINE.

By F. P. DWYER, D.Sc.

*Manuscript received, August 8, 1949. Read, September 7, 1949.*

In a previous paper (Dwyer, Humpolettz and Nyholm, 1946) the preparation of the tris o-phenanthroline ruthenium II salts was described, and the potential of the reaction  $\text{Ru}(\text{phenan})_3^{+++} - e' \rightarrow \text{Ru}(\text{phenan})_3^{+++}$  was determined. The potential was found to decrease with increasing acid concentration, and was notably unstable except in concentrated acid solution. The instability was undoubtedly due to auto-reduction of the oxidant ion, since the blue solution of the oxidised material became orange red—the colour of the original ruthenium II compound—on standing for a short time. It thus appeared that phenanthroline itself, whether freed by dissociation or bound to the ruthenium, was capable of being oxidised at the high potentials operating in the weakly acid solutions. The potential of the system in 0.1 normal acid, 1.29 volts, was lower than that found for the corresponding 2:2' dipyridyl compound (Steigman, Birnbaum and Edmonds, 1942), although by analogy with the ferrous compounds (Dwyer and McKenzie, 1947) the phenanthroline complex was expected to have the higher value.

With small samples of various substituted derivatives of 2:2' dipyridyl and o-phenanthroline, made available by Dr. A. Albert, a further study has been made of the ruthenium compounds, and at the same time the potentials of the 2:2' dipyridyl and o-phenanthroline complexes themselves have been determined by a more reliable procedure. Although the evaluation of redox potentials by the titrimetric method does not give highly accurate results (Dwyer, Nyholm and McKenzie, 1944), the instability of the oxidised form of most of the ruthenium complexes precludes the standard procedure of allowing an electrode to come to equilibrium in an equimolar mixture of the pure oxidant and reductant, and hence some titrimetric procedure must be used. The most reliable of such methods due to Smith and Richter (1944) involves the use of an accurately standardised solution of the reductant, to which is added sufficient of the oxidising agent to convert exactly one-half to the oxidised form. The oxidising agent is selected so that its potential is at least 0.2 to 0.3 volt higher than the redox potential of the substance under examination. The potential of a suitable electrode in such a mixture is found to rise rapidly to a maximum, which persists for a variable time depending on the stability of the oxidised form. The maximum potential represents the most probable value of the true redox potential. In the present study this method has been used for the ruthenium II complexes with 2:2' dipyridyl and o-phenanthroline, but with the substituted derivatives which were available in only small amounts the usual titrimetric method was used.

It has been found that, over a wide range of acidities, the complex with o-phenanthroline had always a slightly higher potential than the 2:2' dipyridyl complex. The substituted derivatives followed the same trend with ruthenium

as with ferrous iron (Smith and Richter, *loc. cit.*). Thus the presence of methyl substituents, which raise the basicity of the chelate group, lowered the potential; whilst bromo substituents which have the opposite effect on the basicity, raised the potential. The presence of methyl substituents in both the parent bases lowered the stability of the oxidised form of the complex, probably by oxidation of such groups. The complex derived from 5-bromo o-phenanthroline, which had the extremely high redox potential of 1.41 volts, was the most unstable of all in the oxidised form. In this compound it is possible that the phenanthroline ring is attacked at the high potential.

### EXPERIMENTAL.

*Ruthenium II Complexes.* These were prepared in a similar manner to the tris-o-phenanthroline compound, described previously (*loc. cit.*) by refluxing an aqueous solution of potassium pentachloro-hydroxy ruthenate IV (1 mol.), with the base (3 mols.), until a greenish brown solution resulted, and then adding a few drops of 30% hypophosphorous acid just neutralised with caustic soda. The heating was continued until the colour had changed to deep orange red, when the mixture was filtered, and potassium iodide added. The compounds then crystallised in orange to orange-red needles or prisms. They were recrystallised from hot water, and dried over concentrated sulphuric acid. The bases used were 2:2'-dipyridyl, 4:4'-dimethyl-dipyridyl, 5:5'-dimethyl-dipyridyl, 5-methyl-o-phenanthroline, 5-bromo-o-phenanthroline and 5-nitro-o-phenanthroline. Tris-5-bromo-o-phenanthroline ruthenium II iodide could not be obtained pure, presumably owing to reduction of the nitro group by the sodium hypophosphite. Under the conditions of drying employed, the compounds derived from 2:2'-dipyridyl and its substituted derivatives were the pentahydrates, whilst those derived from o-phenanthroline were tetrahydrates.

TABLE I.  
*Ruthenium Compounds:  $RuB_3I_2 \cdot 4$  or  $5H_2O$ .*

Base.	M.P.	Calculated.			Found.		
		C.	H.	N.	C.	H.	N.
2:2' dipyridyl .. ..	71°	39.4	3.45	8.98	39.3	3.4	9.1
4:4' (CH <sub>3</sub> ) <sub>2</sub> dipy. ..	169°	43.28	4.59	8.42	43.4	4.3	8.5
5:5' (CH <sub>3</sub> ) <sub>2</sub> dipy. ..	114°	43.28	4.59	8.42	43.2	4.7	8.6
5-CH <sub>3</sub> -o-phen. .. ..	112°	46.35	3.75	8.32	46.4	3.5	8.3
5-bromo-o-phen... ..	117°	35.85	2.40	6.97	35.7	2.3	7.2

The iodides were transformed to the more soluble nitrates by dissolving in a small amount of hot water and adding a slight excess of silver nitrate. The mixture was evaporated to dryness to coagulate the silver iodide and to prevent the formation of complexes of the type  $Ru(phenan)_3(AgI_2)_2$ . The mass was then extracted with water, the silver iodide filtered out, and the solution made up to M/200. The nitrates and sulphates of the complexes with 5-bromo and 5-methyl-o-phenanthroline were so sparingly soluble that the solution were made M/400.

*Apparatus and Procedure.* The redox apparatus consisted of a small beaker, fitted with a stopper, carrying a platinum foil electrode, an ammonium nitrate salt bridge, tubes for the ingress and outlet of carbon dioxide, and a micro burette. The potential of the saturated calomel electrode at 15° C. was taken as 0.2500 volt.

The complex ruthenium compound (5 c.c.) was mixed with distilled water, and nitric acid and the total volume made up to 14 c.c. Since the amount of oxidising agent required for half oxidation was 1.0 to 1.2 c.c., the concentration of ruthenium solution at the equimolar point was M/600, except with the 5-bromo and 5-methyl-o-phenanthroline compounds, when it was M/1200. The mixture was stirred with a rapid stream of purified carbon dioxide, and cooled to 0° C. in an ice bath. The oxidising solution of ceric nitrate was 0.02 N approximately, in nitric acid of the same concentration as the ruthenium complex. It was standardised each time immediately before addition to the ruthenium solution, using a fresh solution of ferrous ammonium sulphate as the standard.

The determination of the redox potentials of the 2:2' dipyridyl and o-phenanthroline compounds was made by adding the calculated volume of the oxidising agent for half oxidation as rapidly as possible, and immediately reading the potential on the platinum electrode. The potentials rose rapidly during the first one to two minutes and then remained stationary for a varying time before falling. The highest potential was taken as the redox potential. The potentials of the substituted compounds were obtained by rapid titration until (approximately) the substance was half oxidised, when it was done more slowly, accepting the highest value, and then rapidly to the end point. From the end point titration, the point of half oxidation was calculated in the usual way. Except with the 2:2' dipyridyl compound, which was the most stable, the potentials are not considered more accurate than  $\pm 5$ mv. The results are shown in Table II.

TABLE II.

*The Redox Potentials of the Ruthenium II Complexes with Substituted Derivatives of 2:2' Dipyridyl and o-Phenanthroline in Nitric Acid.*

Acid Concen- tration Normality.	E <sub>n</sub> .					
	2:2' dipy. Volts.	Phenan. Volts.	4:4' (CH <sub>3</sub> ) <sub>2</sub> Dipy. Volts.	5:5' (CH <sub>3</sub> ) <sub>2</sub> Dipy. Volts.	5-(CH <sub>3</sub> ) Phenan. Volts.	5-Br Phenan. Volts.
0.002	1.303	1.31	1.152	1.240	1.29	1.41
0.1	1.288	1.30	1.115	1.208	1.28	1.36
0.3	1.279	1.29	1.096	1.185	—	—
0.5	1.270	1.28	1.087	1.171	—	—
1.0	1.257	1.26	1.070	1.154	—	—
2.0	1.240	1.24	—	—	—	—
3.0	1.222	1.22	—	—	—	—
5.0	—	1.19	—	—	—	—

## SUMMARY.

The redox potentials of the ruthenium II complexes with substituted derivatives of 2:2' dipyridyl and o-phenanthroline have been determined, and a redetermination of the potentials of the complexes with the parent bases have been made. Methyl groups in both bases depress the potential, whilst the potential of the complex with 5-bromo-o-phenanthroline is the highest of all. The ruthenium compounds thus follow the same trend as the ferrous compounds. At equivalent acid concentrations, the redox potentials of tris-o-phenanthroline ruthenium salts is always higher than of the tris-2:2' dipyridyl analogues.



## ACKNOWLEDGEMENTS.

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## THE CHEMISTRY OF RUTHENIUM.

### PART IV. THE POTENTIAL OF THE QUADRIVALENT/TRIVALENT RUTHENIUM COUPLE IN HYDROCHLORIC AND HYDROBROMIC ACIDS.

By J. R. BACKHOUSE, M.Sc.,  
and F. P. DWYER, D.Sc.

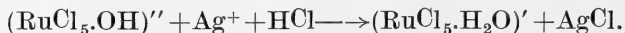
*Manuscript received, August 8, 1949. Read, September 7, 1949.*

Grube and Fromm (1941) investigated the potential of the quadrivalent/trivalent ruthenium couple in a limited range of hydrochloric acid concentrations, and found that it varied from 0.858 volt in 2 normal acid to 0.908 volt in 0.5 normal acid. It was concluded that the reaction was not the simple  $\text{Ru}^{4+} + e' \rightarrow \text{Ru}^{3+}$ ; but hydrogen and chloride ions were also involved. A study of the quadrivalent/trivalent osmium couple in hydrobromic acid (Dwyer, McKenzie and Nyholm, 1946) and in hydrochloric acid (Dwyer, Humpoletz and Nyholm, 1947a) showed that whilst the potentials in hydrobromic acid were usually much lower, when the acid concentrations became small, they coincided. From this observation and the shapes of the curves it was concluded that the reaction measured in low acid concentrations was  $\text{OsO}^{++} + e' \rightarrow \text{OsO}^+$ .

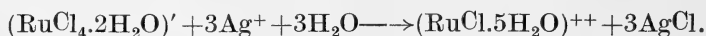
The quadrivalent/trivalent ruthenium couple has now been investigated over a wide range of acid concentrations of hydrochloric and hydrobromic acids in order to determine whether a similar reaction might not apply.

As with quadrivalent osmium, simple salts of quadrivalent ruthenium do not exist. The complex hexahalogenates  $\text{R}_2\text{RuX}_6$  ( $\text{X}=\text{Cl}, \text{Br}$ ), the analogues of the osmium complexes used, are decomposed even in strongly acid solutions, and the hydroxypentahalogenates,  $\text{R}_2(\text{RuX}_5\text{OH})$  result. It is probable that in very dilute acid further replacement of the halogen by hydroxyl may result, but definite compounds have not been isolated.

Trivalent ruthenium is normally obtained by treatment of the quadrivalent compounds with alcohol, sulphurous acid, or stannous chloride, or by cathodic reduction. The present authors have found silver wool especially satisfactory, as the silver halide is precipitated and easily removed.

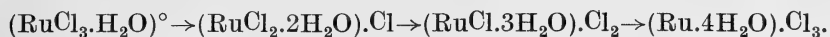


Two series of complex salts result,  $\text{R}(\text{RuCl}_4\cdot 2\text{H}_2\text{O})$ , of which the free acid  $\text{H}(\text{RuCl}_4\cdot 2\text{H}_2\text{O})$  has been isolated in green *cis* and red *trans* forms (Charonnat, 1931), and the pentahalogenoaquo complexes,  $\text{R}_2(\text{RuCl}_5\text{H}_2\text{O})$  (Charonnat, *loc. cit.*; Howe, 1927). In both compounds the molecules of water are firmly bound, whilst Buividate (1935), operating with the ammonium salt of the red series, found that excess of silver nitrate would precipitate only three of the four halogen atoms. The reaction involved was probably



However, Grube and Nann (1939), by evaporating a solution of ruthenium trichloride over concentrated sulphuric acid in high vacuum, or in a current of dry hydrochloric acid at high temperatures isolated the monohydrate,  $\text{RuCl}_3\cdot \text{H}_2\text{O}$ , which they concluded demonstrated the tetravalency of ruthenium III. It was suggested that when solutions of this substance in dilute hydrochloric acid

were allowed to stand successive additions of aquo groups took place according to the scheme



From conductivity experiments and titration with silver nitrate it was found that the first compound contained no ionisable halogen, but on standing not much more than one chlorine atom was ionised, so that the last stage of the scheme is very doubtful. It is difficult to reconcile the conflicting data of Buivide and Grube and Nann on this point, but it may be concluded that at least one chlorine atom is non-ionisable in ruthenium trichloride, and very probably two, since Buivide used an excess of silver nitrate.

Grube and Fromm (1940) also claimed the existence of the diaquo compound above in *cis* and *trans* forms. This claim was made on the observation that greenish solutions of the compound on standing became brown without any increase in the conductivity or precipitable halogen. There is a multitude of evidence, however, for the preferred hexacovalency of trivalent ruthenium (Charonnat, *loc. cit.*; Morgan and Burstall, 1936; Werner and Smirnoff, 1920; Dwyer, Humpoletz and Nyholm, 1947*b*), and these various aquo salts, if they exist, should thus be formulated as are the aquo chromium III chlorides. The alleged green isomer is thus the *cis* form of the octahedral complex  $[\text{RuCl}_2.4\text{H}_2\text{O}]^+$ , or alternatively due to traces of blue ruthenium II salts obtained by carrying the reduction too far.

In this study, the oxidising solution of the hydroxypentahalogeno ruthenate IV was made up to a specified volume by the addition of acid or various salts, and distilled water and freed from oxygen by the passage of carbon dioxide. The reductant solution was made from a fresh portion of the oxygen-free oxidant solution by reduction with silver wool in an atmosphere of carbon dioxide. After mixing, the equimolar solution of oxidiser and reducer was allowed to reach equilibrium among the various ions for two weeks. During this period the potential usually fell slightly, indicating that oxidation of the ruthenium III had not occurred. The potential was measured with two independent electrodes of gold and smooth platinum, which at equilibrium gave the same potential within 0.2 millivolt. The system was badly "poised", and measurement with the ordinary potentiometer was not possible; but with a valve potentiometer steady reproduceable potentials were obtained.

In the presence of hydrochloric acid the potential of the system (using potassium pentachlorohydroxy ruthenate IV as the oxidant) rose rapidly, reaching a maximum at about 0.3 N acid and then decreased sharply (Table I, Curve I). The initial sharp rise in the potential can be ascribed to the reversal of the hydrolysis of the oxidant ion, since the addition of neutral salts such as ammonium sulphate to the weakly acid solution precipitated the colloidal black ruthenium dioxide. The subsequent decrease in the potential leads to the conclusion that the ionic species present in the dilute acid are chiefly cations which are gradually transformed into complex ions.

In the presence of hydrobromic acid (using potassium pentabromohydroxy ruthenate IV as the oxidant), the potential showed also a sharp rise, followed by a marked decrease. However, the potential was always much lower than in the chloride system (Table II, Curve II). It can be concluded, therefore, that unlike the osmium III/osmium IV system, different ionic species exist in the two acids, and that halogen is bound to the metal. The lower potential in hydrobromic acid is consistent with the more pronounced covalent bonding of the bromine atom.

Conclusive evidence for the pronounced effect of the halogen ion on the potential in the chloride system was obtained by a series of measurements, in which the effects of hydrogen ion, chloride ion and ionic strength were studied

TABLE I.  
*The Effect of Hydrochloric Acid on the Ru<sup>IV</sup>/Ru<sup>III</sup> Potential.*  
 (Cf. Curve I, Fig. 1.)

Acid Concentration. Normality.	E, Observed. (Volt.)	E <sub>n</sub> . (Volt.)
0.2	0.674	0.918
0.25	0.688	0.932
0.325	0.678	0.922
0.423	0.675	0.919
0.596	0.661	0.905
0.77	0.649	0.893
0.94	0.637	0.881
1.46	0.608	0.852
2.5	0.557	0.801
3.53	0.520	0.764
4.57	0.490	0.734
5.47	0.470	0.714

TABLE II.  
*The Effect of Hydrobromic Acid on the Ru<sup>IV</sup>/Ru<sup>III</sup> Potential.*  
 (Cf. Curve II, Fig. 1.)

Acid Concentration. Normality.	E, Observed. (Volt.)	E <sub>n</sub> . (Volt.)
0.2	0.491	0.735
0.25	0.531	0.775
0.472	0.503	0.747
0.916	0.480	0.724
2.03	0.436	0.680
3.58	0.395	0.639
4.25	0.380	0.624
6.02	0.357	0.601
6.91	0.340	0.584

separately. With fixed chloride ion concentrations of 0.025 N and 1.115 N the hydrogen ion concentration was increased by means of sulphuric acid (Tables III, IV, Curves III, IV). In each series the potential decreased with increasing hydrogen ion concentration, but the decrease was much smaller than with hydrochloric acid. When the hydrogen ion concentration was kept constant at 0.25 N and 1.115 N in the next series of measurements and the chloride ion concentration increased with potassium chloride, the potential decreased sharply, the curves being only slightly higher than the hydrochloric acid curve (Tables V, VI, Curves V, VI). The increase in ionic strength was made at fixed hydrogen and chloride ion concentrations by the addition of ammonium sulphate. The decrease in the potential was relatively small (Table VII).

The decrease in the potential of a redox system by the addition of neutral salts can usually be ascribed either to the disproportionate reduction of the activity of the oxidiser, by reason of its greater charge in cationic systems (such as the ferric/ferrous system), or to complex ion formation with the oxidiser. In an anionic system involving complex metallic ions, the reductant usually carries the greater charge as in the ferricyanide/ferrocyanide system (Kolthoff

TABLE III.

*The Effect of Hydrogen Ion Concentration on the Ru<sup>IV</sup>/Ru<sup>III</sup> Potential.  
Chloride Ion Concentration, 0.25 N.  
(Cf. Fig. 2, Curve III.)*

Total Hydrogen Ion Concentration Normality.	E, Observed. (Volt.)	E <sub>h</sub> . (Volt.)
0.25	0.688	0.932
0.505	0.701	0.945
0.76	0.699	0.943
1.015	0.699	0.943
1.52	0.693	0.937
2.54	0.680	0.924
3.65	0.671	0.915
4.36	0.660	0.904
6.63	0.612	0.856

TABLE IV.

*The Effect of Hydrogen Ion Concentration on the Ru<sup>IV</sup>/Ru<sup>III</sup> Potential.  
Chloride Ion Concentration, --5 N.  
(Cf. Fig. 2, Curve IV.)*

Total Hydrogen Ion Concentration Normality.	E, Observed. (Volt.)	E <sub>h</sub> . (Volt.)
1.115	0.629	0.873
2.135	0.617	0.861
3.155	0.602	0.846
4.17	0.584	0.838
6.22	0.557	0.803

TABLE V.

*The Effect of Chloride Ion Concentration on the Ru<sup>IV</sup>/Ru<sup>III</sup> Potential.  
Hydrogen Ion Concentration, 0.25 N.  
(Cf. Fig. 2, Curve V.)*

Total Chloride Ion Concentration, Normality.	E, Observed. (Volt.)	E <sub>h</sub> . (Volt.)
0.25	0.688	0.932
0.425	0.695	0.939
0.687	0.671	0.915
1.125	0.646	0.890
1.65	0.620	0.864
2.26	0.598	0.842

and Tomsicek, 1935) and the chloriridate/chlororidite and bromiridate/bromiridite systems (Dwyer, McKenzie and Nyholm, 1944, 1947c). As a result, the potential rises with increasing ionic strength. It is evident that in determining the constitution of a redox system the effects of both complex ion formation and the ionic strength must be considered.

TABLE VI.

*The Effect of Chloride Ion Concentration on the Ru<sup>IV</sup>/Ru<sup>III</sup> Potential.  
Hydrogen Ion Concentration, 1.115 N.  
(Cf. Fig. 2, Curve VI.)*

Total Chloride Ion Concentration, Normality.	E, Observed. (Volt.)	E <sub>h</sub> . (Volt.)
1.115	0.629	0.873
1.64	0.602	0.846
2.17	0.580	0.824
3.13	0.556	0.800

TABLE VII.

*The Effect of Ammonium Sulphate on the Ru<sup>IV</sup>/Ru<sup>III</sup> Potential.*

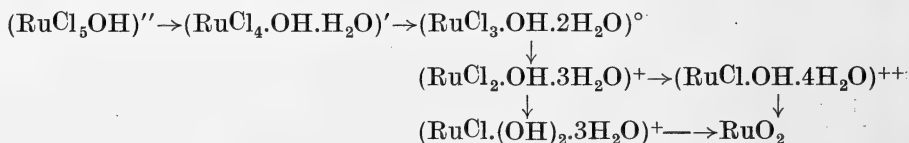
Hydrochloric Acid Concentration Normality.	E <sub>h</sub> . (Volt.)	Total Normality with Ammonium Sulphate.	E <sub>h</sub> . (Volt.)
0.77	0.893	1.27	0.889
0.94	0.881	2.45	0.869
1.46	0.852	3.98	0.839

It can be assumed from general principles that the reductant is the more cationic, and from the observations of Buividate and Grube and Nann (*loc. cit.*) it is probable that the ion present in dilute solution is the hydrated (RuX<sub>2</sub>)<sup>+</sup> or less, probably (RuX)<sup>++</sup>. With increasing halogen ion concentration there will be a tendency for the formation of complex anions such as (RuX<sub>4</sub>.2H<sub>2</sub>O)' and (RuX<sub>5</sub>.H<sub>2</sub>O)'', but the stability of such ions, if the usual rule is followed, will be much smaller than similar complex anions formed by the oxidant, and their effect can thus be neglected. The separation of black ruthenium dioxide from solutions of potassium pentachlorohydroxy ruthenate IV in very dilute acid leads to the conclusion that this salt can undergo progressive dissociation. Observations on the colour of solutions of the bromo compound in various concentrations of hydrobromic acid supports this view. Thus the deep purple colour in normal hydrobromic acid gradually becomes lighter and brownish in colour-like dilute solutions of the chloro compound—as the acid is diluted and finally darkens with the separation of ruthenium dioxide. If the acid concentration is raised above 3.5 normal, the purple colour changes to brown, suggesting the replacement of the hydroxyl group by bromine has occurred.



This latter reaction cannot be performed on the chloro compound with even concentrated hydrochloric acid.

The progressive dissociation of the chloro compound can be expected to follow a scheme such as



The dissociation of the initial compound can be repressed by direct replacement of aquo and hydroxyl groups by chloride ions, the latter replacement being facilitated by hydrogen ions.

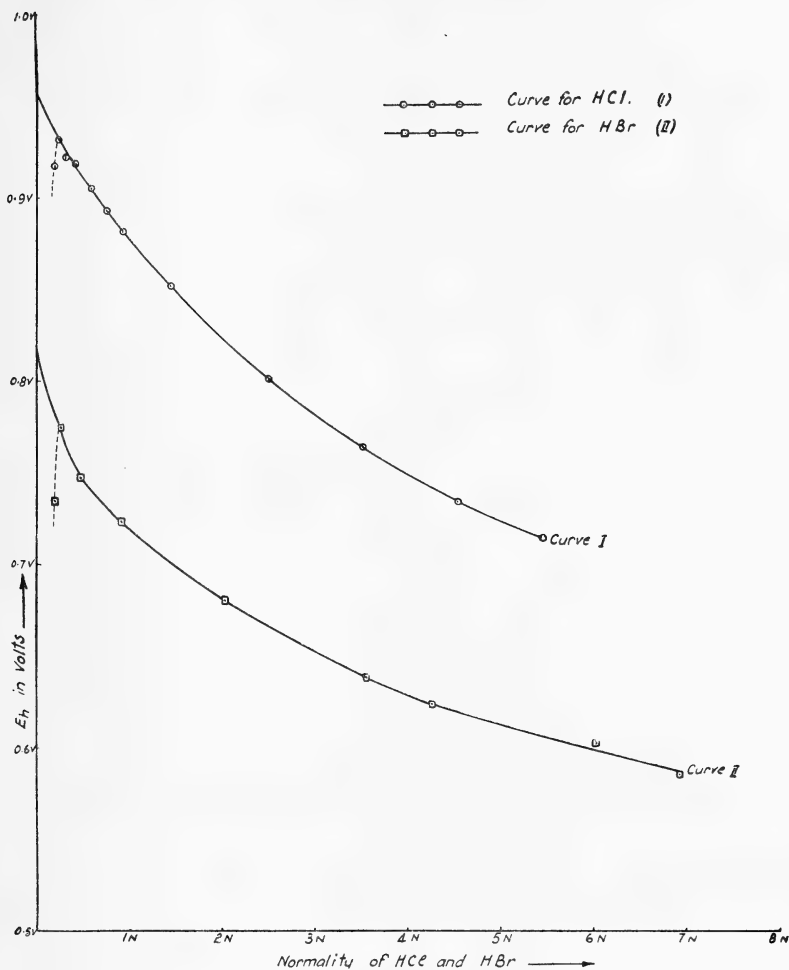
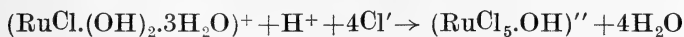
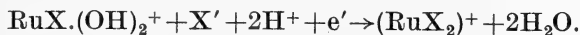


Fig. 1.

It is considered that the potential measured in dilute acid at the point where the maximum is reached is of the reaction



The potential extrapolated from this point to zero acid concentration, for the chloride system was  $0.96 \pm 0.002$  volt, and for the bromo system  $0.82 \pm 0.002$  volt.

## EXPERIMENTAL.

*Oxidant and Reductant Solutions.*

Potassium pentachlorohydroxy ruthenate IV was prepared by the method of Charonnat (*loc. cit.*) from the pure metal. The purplish brown crystals were recrystallised from normal hydrochloric acid, and dried in vacuum over sulphuric acid. The oxidant solution was made in oxygen-free normal hydrochloric acid, and was M/100. Solutions in 0.1 N acid darkened slightly on keeping, but in 0.20 N acid ruthenium dioxide gradually precipitated.

(b) *Potassium aquopentachloro ruthenate III* was prepared by taking a portion of the oxidant solution above, and allowing it to stand in an atmosphere of carbon dioxide in contact with silver

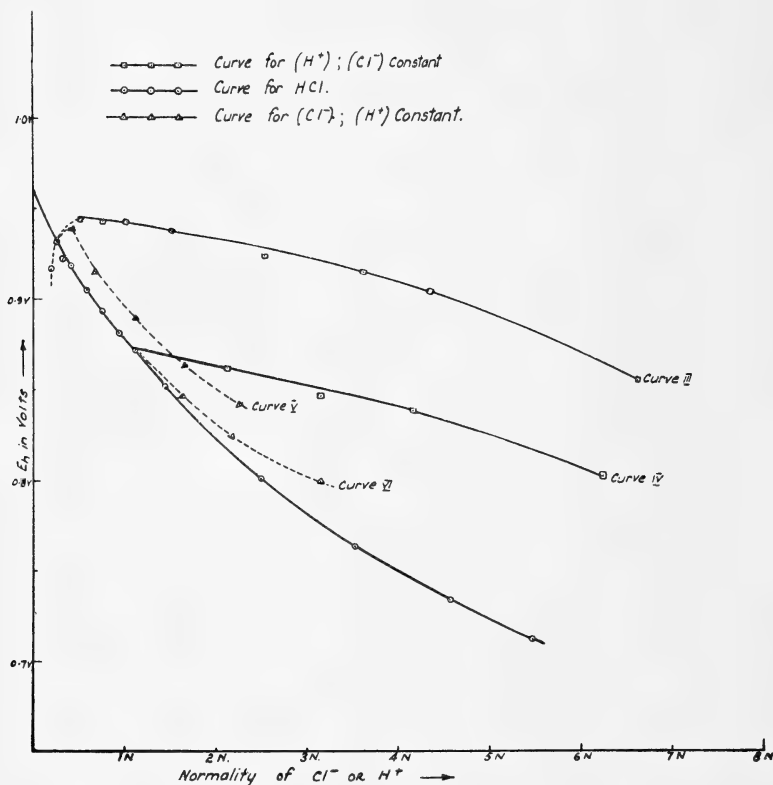


Fig. 2.

wool. At the end of twenty-four hours, the colour had changed to yellow, and the precipitate of the silver halide had settled out. No trace of ruthenium metal was formed during the reduction. The reduced solution was kept over silver wool in the inert atmosphere.

(c) *Potassium pentabromohydroxy ruthenate IV*. This substance was prepared by the same method as the chloro compound, either by treatment of the potassium ruthenate with hydrobromic acid, or by fusion of ruthenium metal with potassium hydroxide and potassium bromate, followed by extraction with water and treatment with hydrobromic acid. The dark purplish brown crystals were recrystallised from dilute hydrobromic acid. The M/100 solution was made in normal hydrobromic acid.

(d) *Potassium aquopentabromo ruthenate III*. The reduction of the purple oxidant solution could not be performed with alcohol in the presence of hydrobromic acid, whilst in the absence of acid or in very dilute acid, hydrolysis caused the deposition of some ruthenium dioxide.



Reduction with silver wool gave the required pale yellow solution of the compound, but the reduction tended to form some bivalent ruthenium compound owing to the low potential of the reaction  $\text{Ag} + \text{Br}' \rightarrow \text{AgBr} \text{ e}'$ . However it was found that the colour change from yellow to the pale green of the ruthenium II compound was quite sharp, and thus by the addition of some of the oxidant solution it was possible to remove the bivalent state. The solution was stored in an atmosphere of carbon dioxide.

*Apparatus.* The redox assembly, with a saturated potassium chloride salt bridge, was the same as that used in previous determinations (Dwyer, McKenzie and Nyholm, 1944). The potential of the saturated calomel electrode was taken as 0.2443 volt at 25° C. The potentials on gold and platinum electrodes were measured on a Leeds and Northrup valve potentiometer, and are considered accurate to  $\pm 2\text{mv}$ .

*Procedure.* The oxidant solution (5 ml.) was mixed with acid, and distilled water in that order to prevent hydrolysis and made up to 35 ml. Where potassium chloride and ammonium sulphate were added, the dry salts were used, and dissolved at room temperature. The hydrobromic acid was freshly distilled, free from bromine, and was stored over carbon dioxide. The prepared solution was freed from traces of air by passage of carbon dioxide and the reductant solution (5 ml.) added. The final mixture was thus M/800 with respect to both oxidant and reductant. It was allowed to stand in an inert atmosphere for two weeks. When equilibrium had been established among the various ions, the mixture was placed in the redox vessel, previously filled with carbon dioxide, and allowed to come to equilibrium with the electrodes. During this time—usually 24 hours—the potential decreased slightly. Finally the salt bridge was inserted, and the equilibrium potential measured whilst the solution was stirred with a current of carbon dioxide. The results of the various measurements are shown in the foregoing tables and curves.

#### SUMMARY.

The potential of the quadrivalent/trivalent ruthenium couple has been studied in hydrochloric and hydrobromic acid solutions. From the shapes of the curves it is concluded that the system is cationic. The potential is depressed markedly by halide ions and to a lesser extent by hydrogen ions. The results are consistent with the existence of hydrated cations of the type  $(\text{RuX}(\text{OH})_2)^+$  and  $(\text{RuX}.\text{OH})^{++}$  for the oxidant and  $(\text{RuX}_2)^+$  and  $(\text{RuX})^{++}$  for the reductant. The potentials for the chloro and bromo systems respectively, extrapolated from the point where hydrolysis becomes serious to zero acid concentrations are  $0.96 \pm 0.002$  volt and  $0.82 \pm 0.002$  volt.

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VOLUME LXXXIII

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PART III

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## THE CHEMISTRY OF RUTHENIUM.

### PART V. THE POTENTIAL OF THE BIVALENT/TRIVALENT RUTHENIUM COUPLE IN HYDROCHLORIC ACID.

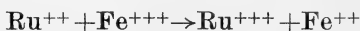
By J. R. BACKHOUSE, M.Sc.,  
and F. P. DWYER, D.Sc.

*Manuscript received, August 8, 1949. Read, September 7, 1949.*

When a solution of potassium pentachlorohydroxy ruthenate IV in hydrochloric acid is treated with strong reducing agents such as zinc or lead, the deep brown colour changes successively to yellow, green, blue, and finally deposits the metal itself. The yellow solution contains trivalent ruthenium (Howe, 1927 ; Charonnat, 1931), but for a time a controversy existed over the green and blue substances, which were thought to contain respectively bivalent and monovalent ruthenium. According to Latimer (1940) the question has been definitely settled by the work of Crowell and Yost (1928), who showed that the blue solution contained the element in the bivalent state, whilst the green colour was due to a mixture of the trivalent and bivalent states. Recently, however, Grube and Nann (1939), as a result of the study of the electrolytic reduction of ruthenium trichloride in hydrochloric acid, claimed that the reduction proceeded to the bivalent state in concentrated acid, but in dilute acid the univalent state resulted. The reduction steps were identified by potentiometric titration with hydrogen peroxide. Univalent ruthenium was found to undergo disproportionation— $2\text{Ru}^+ \rightarrow \text{Ru}^{++} + \text{Ru}$ ; and the potential of the reaction  $\text{Ru}^+ - e' \rightarrow \text{Ru}^{++}$  was found to be in the range 0.03 to 0.05 volt. The published titration curves, however, do not show well-marked inflexions; the potentials from which the curves were obtained were almost instantaneous and not equilibrium values, and an irreversible oxidant was used. Additional evidence in substantiation of univalent ruthenium is therefore desirable.

The present investigation deals with the determination of the potential of the bivalent/trivalent ruthenium couple in hydrochloric acid with a view to checking the existence of the univalent state.

The mixed oxidant/reductant solution was prepared by the reduction of potassium pentachlorohydroxy ruthenate IV in hydrochloric acid with pure lead foil in an oxygen-free atmosphere of carbon dioxide. The resulting deep blue solution contained 15–20% of bivalent ruthenium, whilst the remainder was trivalent. Although the lack of equimolarity in this solution involved a large correction to obtain the standard potential, the large excess of the trivalent state automatically eliminated the possibility of any of the alleged monovalent state being present. The reduced solution to which varying amounts of acid were added was allowed to come to equilibrium with a smooth gold electrode in an atmosphere of carbon dioxide. As soon as the potential reading was taken the concentration of bivalent ruthenium was determined by addition of a known volume of the solution to oxygen-free ferric alum solution. In this way an equivalent amount of ferrous salt was formed.



From the present work it is known that the potential of the  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  system is of the order of 0.1 volt, whilst from the previous paper (This Series,



Part III) the potential of the  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$  system is approximately 0.9 volt, hence the ferric salt can only oxidise to the trivalent state. The partly reduced iron solution was then oxidised potentiometrically with potassium permanganate, the first step being due to oxidation of the ferrous ion. The total ruthenium in the solution was estimated by oxidation to the quadrivalent state with a slight excess of chlorine, followed by potentiometric titration with stannous chloride. The potential of the stannous/stannic system (0.13 volt; Latimer, 1940) is such that the reduction  $2\text{Ru}^{4+} + \text{Sn}^{++} \rightarrow 2\text{Ru}^{3+} + \text{Sn}^{4+}$  proceeds to completion without the formation of any bivalent ruthenium compound, or the separation of ruthenium metal. The difference in the total ruthenium concentration and the bivalent ruthenium concentration then gives the concentration of trivalent ruthenium.

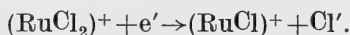
The observed potentials were corrected to the standard equimolar potential by the usual equation. Since the activities of the oxidant and reductant were unknown, the observed concentrations were substituted.

The reduction of ruthenium tribromide in hydrobromic acid could be effected with either silver or lead, but the reduced solution was coloured green. Even when the reduction was carried out with zinc to the point where most of the metal was deposited, the colour remained green. It was concluded that the green colour was not due to admixture of the bivalent and trivalent states, but that the ionic species of bivalent ruthenium is not the simple hydrated  $\text{Ru}^{++}$  but hydrated  $(\text{RuBr})^+$  and  $(\text{RuCl})^+$ . The determination of the potential of the green solution was not successful as a brown deposit formed on the electrode, whilst a satisfactory method could not be found for the estimation of the bivalent ruthenium. The potential of the trivalent/quadrivalent ruthenium couple in hydrobromic acid (approx. 0.7 volt) is almost the same as the ferrous/ferric system. The reaction  $\text{Ru}^{++} + \text{Fe}(\text{CN})_6^{''''} \rightarrow \text{Ru}^{3+} + \text{Fe}(\text{CN})_6^{'''}$ , although theoretically feasible, proved to be unsuitable.

The potential of the chloride system was found to be almost independent of the acid concentration from 1.5 N to 6.8 N hydrochloric acid. Measurements in the lower acid concentrations could not be obtained owing to the separation of ruthenium on the electrode



From the independence of the potential on the ionic strength, it can be concluded that increasing ionic strength has the same effect on the activities of both the oxidant and the reductant, and hence that they probably carry the same charge. Since the lowest valencies of the metal are involved, the system is almost certainly cationic, and the equivalence of charge must be due to covalent bonding of part of the halogen. In Part III of this series evidence was put forward for the existence of ruthenium trichloride in dilute solution as either the hydrated ion  $(\text{RuCl})^{++}$  or  $(\text{RuCl}_2)^+$ , and from the behaviour of ruthenium tribromide towards reducing agents it is suggested that the reductant ion is  $(\text{RuCl})^+$ . It is considered, therefore, that the redox reaction of the couple is



The potential of the trivalent/bivalent couple in 1.53 N acid, 0.084 volt is not very much higher than the potential of the alleged bivalent/monovalent couple measured by Grube and Nann (*loc. cit.*)—0.03 to 0.05 volt in 0.1 N acid. In solution containing small concentrations of hydrochloric acid, ruthenium trichloride is known to hydrolyse extensively (Grube and Fromm, 1940). As a result the potential of the  $\text{Ru}^3/\text{Ru}^2$  system can be expected to be quite low in low concentrations of hydrochloric acid. It is also significant that the disproportionation, which was supposed to be due to univalent ruthenium, occurs with bivalent ruthenium in weakly acid solution. This could well arise by dissociation of the  $(\text{RuCl})^+$  ion to  $\text{Ru}^{++}$ , which undergoes disproportionation.

It is concluded from the present study that the univalent ruthenium ion has no existence in solution.

### EXPERIMENTAL.

#### *Oxidant and Reductant Solutions.*

An M/50 solution of potassium pentachlorohydroxy ruthenate IV in hydrochloric acid (2 N) was saturated with oxygen-free carbon dioxide and thin strips of lead foil added. After about thirty minutes the deep brown solution had become yellow and the reaction had almost stopped by the deposition of ruthenium on the lead. The solution was decanted on to fresh lead, and sealed in carbon dioxide until after 20–30 minutes a deep royal blue solution had formed. This was filtered from lead chloride and ruthenium metal through a sintered glass filter into a storage vessel, fitted with a burette, so that known volumes could be withdrawn without exposure to oxygen. Since the acid concentration had changed during the reduction by reaction with the lead, the acidity was determined by titration with sodium hydroxide and methyl orange indicator. The total ruthenium in the solution was estimated by dilution of a known volume with dilute hydrochloric acid and oxidation with a slight excess of chlorine water. The excess was then boiled out, and the solution potentiometrically titrated with standard stannous chloride. The excess of chlorine was such that any loss as ruthenium tetroxide could be regarded as negligible. The solution was found to be M/800 with respect to ruthenium.

#### *Apparatus.*

The redox apparatus was the same as that used in previous determinations (Dwyer, McKenzie and Nyholm, 1946). The saturated calomel electrode, taken as 0.2443 volt at 25° C., was connected to the cell through a saturated potassium chloride salt bridge. During the potential determinations the apparatus was sealed with apeizon wax and kept under a slight pressure of carbon dioxide.

#### *Procedure.*

An oxygen-free solution (30 ml.) of hydrochloric acid of the required concentration was saturated with carbon dioxide in the redox vessel, the reduced ruthenium solution (10 ml.) added quickly, and the apparatus sealed. After approximately 24 hours equilibrium had been attained, and the potential was measured with a Leeds and Northrup valve potentiometer. The system was unpoised and the ordinary potentiometer was unreliable. A portion of the solution (30 ml.) was immediately withdrawn through a stream of carbon dioxide and added to oxygen-free standard ferric alum solution. Potentiometric titration with potassium permanganate then gave the concentration of bivalent ruthenium at the equilibrium point.

The potential values at the various acid concentrations are shown in Table I.

TABLE I.  
*The Potential of the Ru<sup>II</sup>/Ru<sup>III</sup> System in Hydrochloric Acid.*  
*Total Ru Concentration,  $1.25 \times 10^{-3}$  M.*

Acid Concentration Normality.	E, Observed. (Volt.)	[Ru <sup>++</sup> ] $\times 10^{-3}$	[Ru <sup>+++</sup> ] $\times 10^{-3}$	E, Observed Corrected. (Volt.)	E <sub>h.</sub> (Volt.)
1.53	—0.128	0.279	0.97	—0.160	0.084
2.6	—0.130	0.301	0.95	—0.160	0.084
2.6	—0.132	0.305	0.945	—0.161	0.083
3.64	—0.121	0.27	0.98	—0.154	0.090
5.22	—0.131	0.27	0.98	—0.164	0.080
6.8	—0.127	0.28	0.97	—0.157	0.087

## SUMMARY.

The potential of the bivalent/trivalent ruthenium couple in hydrochloric acid was found to be  $0.084 \text{ volt} \pm 0.005 \text{ volt}$  in the hydrochloric acid range of concentrations from 1.53 N to 6.8 N. It is considered that the system is cationic with the ionic species  $(\text{RuCl}_2)^+$  and  $(\text{RuCl})^+$  for the oxidant and reductant respectively. From the potential values and the behaviour of the system in low acid concentrations, it is concluded that Grube and Nann's alleged univalent ruthenium is really bivalent ruthenium.

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# KEPLER'S PROBLEM.

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**Abstract.**—Kepler's problem is reviewed from analytical and numerical standpoints, the region of usefulness of various solutions defined and formulae suggested for the nearly parabolic case. A bibliography is given.

The two body problem was solved (kinematically) by Kepler with the enunciation of his three laws of planetary motion which were later to be contained within the implications of the more general theory of gravitation. The Keplerian rules (regarded as derived from the gravitational equations) are still used in most derivations of the equations which connect the position variables of planetary motion with the time variable. The problem of finding the coordinates of a planet in the plane of its orbit in unperturbed motion is Kepler's problem.

If we express the equation of the solution path of planetary motion in a form using the parameters  $e$  (eccentricity) and  $q$  (perihelion distance) which apply equally to the three conics without involving infinite or imaginary values (as for example the major and minor axes would) and take  $x_0, y_0$  as the rectangular coordinates in the plane of motion with the  $x_0$  axis directed towards perihelion we obtain

$$x_0^2 + y_0^2 = \{q(1+e) - ex_0\}^2 \quad (1)$$

The equation for constancy of areal velocity is

$$x_0 y'_0 - x'_0 y_0 = c$$

that is

$$2x_0 y'_0 - (x_0 y_0)' = c$$

where the dashes indicate differentiation with regard to time.

Now if we write

$$\lambda = \frac{x_0}{q}, \quad \mu = \frac{y_0}{q} \quad \text{and} \quad \varepsilon = \frac{1-e}{1+e} \quad (2)$$

and take the initial point at perihelion this becomes

$$\int_0^{\mu_1} 2q^2 \lambda d\mu - q^2 \lambda_1 \mu_1 = ct \quad (3)$$

and equation (1) gives

$$\lambda = \frac{1}{1-e} \{ -e \pm (1 - \varepsilon \mu^2)^{\frac{1}{2}} \} \quad (4)$$

In substituting (4) into (3) in the elliptic case the branch of  $\lambda$  corresponding to the upper sign must be used from perihelion ( $\mu=0, \lambda=1$ ) to  $\mu=\varepsilon^{-\frac{1}{2}}, \lambda=-e/(1-e)$  and that corresponding to the lower sign from this point to  $\mu=0, \lambda=-\varepsilon^{-1}$ . In the hyperbolic case the lower sign corresponds to the non-solution branch of the hyperbola. The case  $e=1$  is obvious.

On integrating (3) in this way, putting  $c=kq^{\frac{1}{2}}(1+e)^{\frac{1}{2}}$  from the dynamical theory where  $k$  is the Gaussian constant, we obtain

$$k(1+e)^{\frac{3}{2}}q^{-\frac{3}{2}}t = \varepsilon^{-\frac{3}{2}} \{ \pm \sin^{-1} \varepsilon^{\frac{1}{2}} \mu - e \varepsilon^{\frac{1}{2}} \mu \} + C \quad (5)$$

where the subscript on  $\mu$  may now be dropped without ambiguity. In the elliptic case we can without loss of generality take the positive sign and  $C=0$  if we put  $\sin^{-1}\epsilon^{1/2}\mu > \pi/2$  in the interval in which  $\mu$  is decreasing. The hyperbolic case requires only the upper sign.

From (4) we obtain

$$\lambda = 1 - \frac{\mu^2}{1+e} \frac{1 \mp (1-\epsilon\mu^2)^{1/2}}{\epsilon\mu^2}, \quad (6)$$

with the same remarks about signs. This will be found a convenient form for calculation.

Equation (5) will be taken as the general expression of Keplerian motion. If we put  $\epsilon^{1/2}\mu = \sin E$

$$M = ka^{-3/2}t = E - e \sin E, \quad (7)$$

where  $a$  is the semi-major axis,  $M$  the mean anomaly and  $E$  the eccentric anomaly.

When  $\epsilon$  is negative put  $\epsilon = -\alpha = (e-1)/(e+1)$ ,  $\sinh F = \alpha^{1/2}\mu$  and we obtain (since  $\sin^{-1}i\alpha^{1/2}\mu = i \sinh^{-1}\alpha^{1/2}\mu$ )

$$M = ka^{-3/2}t = e \sinh F - F. \quad (8)$$

Equation (5) may be written

$$D = 12k(1+e)^{1/2}q^{-3/2}t = 12\mu + \mu^3(1+\epsilon)6 \left( \frac{\sin^{-1} \epsilon^{1/2}\mu - \epsilon^{1/2}\mu}{\epsilon^{3/2}\mu^3} \right), \quad (9)$$

which will be found a convenient expression for dealing with the nearly parabolic case ( $e$  near 1).

For the parabolic case ( $e=1$ )

$$12\sqrt{2k}q^{-3/2}t = 12\mu + \mu^3 \quad (10)$$

and if we place

$$\tan \frac{v}{2} = \tau = \frac{1}{2}\mu$$

we obtain

$$6k(2q)^{-3/2}t = 3\tau + \tau^3$$

which is the usual expression for parabolic motion, where  $v$  is the true anomaly.

Equation (7) is the one which now bears Kepler's name. It is an early example of a transcendental equation occurring in applied mathematics and very few men even as eminent as Kepler can have such an enduring memorial as this equation. The necessity for its frequent solution and the difficulties, numerical and analytical, which it presents have kept alive interest in the equation during the whole of the 300 years since its discovery. The analytical points involved if we wish to express the implicit function  $E$  of equation (7) explicitly as a series in  $M$  and  $e$  are of interest and consideration of them has been important in the development of the theory of analytic functions (see references in Wintner, 1941). The interval of convergence as a power series in  $e$  must depend on the singularities of the function  $E=E(e, M)$  in the complex plane for  $e$ .

The function

$$e = \frac{E-M}{\sin E} \quad (11)$$

is a meromorphic function with simple poles at the points  $\sin E=0$  except when  $E=M$ .

The inverse function  $E=E(e, M)$  must be multiple valued and the branch for which  $e=0$  implies  $E=M$ , that is the branch in which we are interested,

is regular at  $e=0$ . The singularities of the inverse function are given by zeros of the derivative, that is by

$$\frac{1-e \cos E}{\sin E}=0$$

The singularities at  $E=\infty$  correspond to connected paths to infinity (see Hurwitz, 1906) in the  $E$  plane for which  $e$ , given by (11), approaches a finite point. This only occurs for  $e=0$  and therefore does not affect the branch in which we are interested, which is regular at this point. Hence the singularities are determined by (11) and the equation

$$M-E+\tan E=0 \quad (12)$$

where  $M$  is real (in the elliptical case).

Every point on the real axis of  $e$  for which  $|e| \geq 1$  is a branch point. Let us put  $E=a+ib$  into equation (12) and equate real and imaginary parts giving

$$\begin{aligned} b &= \frac{(1+\tan^2 a) \tanh b}{1+\tan^2 a \tanh^2 b}, \\ -M+a &= \frac{(1-\tanh^2 b) \tan a}{1+\tan^2 a \tanh^2 b}, \end{aligned} \quad (13)$$

from which

$$\tan^2 a = \frac{\tanh b - b}{(b \tanh b - 1) \tanh b} \quad (14)$$

and

$$(a-M)^2 = (\tanh b - b)(b - \coth b) \quad (15)$$

Equation (15) shows that  $b$  must lie between  $-\beta$  and  $+\beta$  where  $\beta$  is given by

$$\beta = \coth \beta$$

If, using equations (11) and (12), we write

$$\xi + i\eta = e = \sec E,$$

equate real and imaginary parts and use equation (13) we obtain

$$\left. \begin{aligned} \xi &= b \cos a \operatorname{cosech} b, \\ \eta &= b \sin a \operatorname{sech} b. \end{aligned} \right\} \quad (16)$$

If we now use  $b$  as a parameter equations (14) and (16) give the curve of singularities.

For the case of the hyperbola  $M$  is replaced by  $iN$  (with  $N$  real); equation (12) becomes

$$-iN + E - \tan E = 0$$

and any real value of  $e$  for which  $|e| \leq 1$  gives a solution (that is a singularity).

If as before we let  $E=a+ib$ ,  $e=\xi+i\eta$  the equations corresponding to (14), (15) and (16) are

$$\left. \begin{aligned} \tanh^2 b &= \frac{\tan a - a}{(1+\tan a) \tan a}, \\ (b-N)^2 &= (\tan a - a)(\cot a + a) \end{aligned} \right\} \quad (17)$$

and

$$\left. \begin{aligned} \xi &= (b-N) \cos a \operatorname{cosech} b, \\ \eta &= (b-N) \sin a \operatorname{sech} b. \end{aligned} \right\} \quad (18)$$

The curves (symmetrical about both axes) of singularities for the ellipse and the hyperbola are shown in Figure 1, where the dashed line refers to the

ellipse and the dotted line to the hyperbola. The curve for the ellipse was first discussed by T. Levi-Civita (1904*a*) and C. V. L. Charlier (1904) (the work of the latter not having been available to me) and the hyperbola by H. G. Block (1904). Other discussions are given by H. Andoyer (1923) and A. Wintner (1941).

For elliptic motion the nearest singular point to the origin is on the imaginary axis at a point given by

$$\beta = \coth \beta$$

$$\eta = \beta \operatorname{sech} \beta = 0.6627 \dots$$

The power series expression for  $E$  in elliptic motion is convergent uniformly with  $M$  only for  $0 \leq e < 0.6627 \dots$ . In both cases the curve is incident with real axis at an angle of  $\pi/3$  and in the hyperbolic case the curve is asymptotic to the line  $\xi = \pi/2$ .

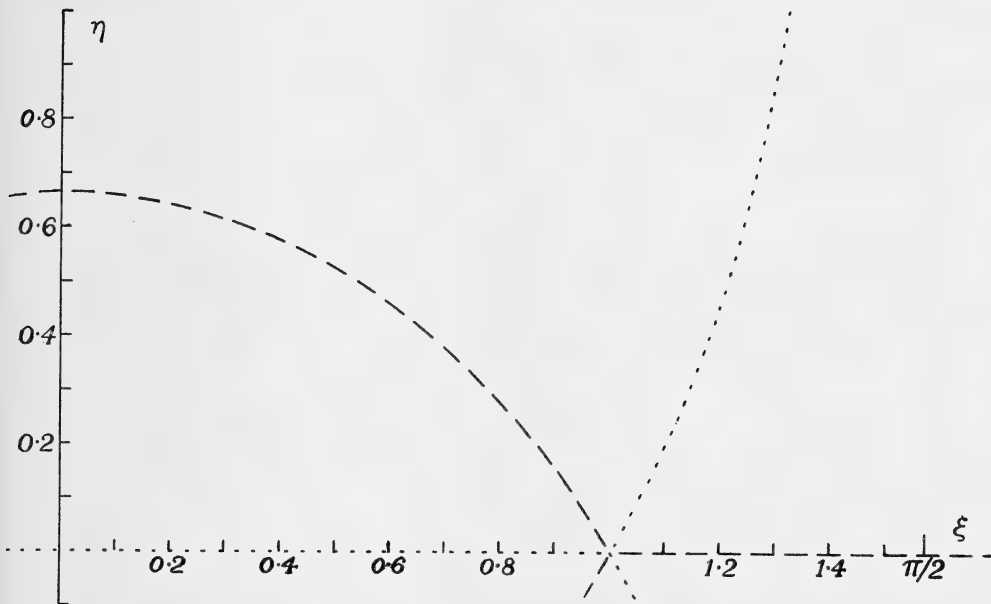


Fig. 1.—Curves of singularities in the complex  $e$  plane (first quadrant) for solutions of elliptical and hyperbolic motion.

In the case of hyperbolic motion the curve of singularities shows that no development in  $e$  or  $1/e$  converges for all values of  $M$  and even the development in powers of  $e - e_0$  ( $e_0 > 1$ ) is of no practical use for the circle of convergence (uniformly with  $M$ ) is limited by the curve and cannot include the region near  $e = 1$ , the cusp of the curve.

Turning to equation (10) for parabolic motion  $\mu$  is seen to be a three valued function of  $D = 12\sqrt{2}kq^{-3/2}t$ . For  $D$  real there are two complex roots and one real, the real root increasing monotonically with  $D$ . The zeros of the first derivative of  $12\mu + \mu^3 + D$  occur at  $\mu = \pm 2i$ ; the Riemann surface of  $\mu = \mu(D)$  has branch points at  $D = \pm 16i$  and there are no further finite singularities. These singularities limit the radius of convergence and the general usefulness of any development of (the real branch of)  $\mu$  according to powers of  $D - D_0$ .

Turning to the nearly parabolic case write equation (9) in the form  $F(\varepsilon, \mu, D)=0$ . Expanding  $\sin^{-1} \varepsilon^{1/2}\mu$  as a series we obtain

$$0 = -D + 12\mu + \mu^3(1+\varepsilon)6\left(\frac{1}{2.3} + \frac{1.3}{2.4} \frac{\varepsilon\mu^2}{5} + \dots\right), \quad (19)$$

where the right-hand member is an expression of part of the branch of  $F(\varepsilon, \mu, D)$  for which  $\mu=0$  implies  $D=0$  (for  $|\varepsilon\mu^2| < 1$ ). For this branch of  $F(\varepsilon, \mu, D)$  the origin is a regular point but it is a pole for every other branch.

Also we have

$$\begin{aligned} \frac{\partial F}{\partial \mu} &= 12 + (1+\varepsilon)\frac{6}{\varepsilon}\{(1-\varepsilon\mu^2)^{-1/2}-1\} \\ &= 12 + \mu^2(1+\varepsilon)6\left(\frac{1}{2} + \frac{1.3}{2.4} \varepsilon\mu^2 + \dots\right). \end{aligned} \quad (20)$$

This shows that for  $D, \varepsilon$  and  $\mu$  real we have

(i) When  $0 \leq \varepsilon < 1$ , the elliptical case, i.e.  $1 \geq \varepsilon > 0$   $F$  is monotonic increasing with  $\mu$  for  $\varepsilon\mu^2 < 1$ ,

(ii) When  $\varepsilon \geq 1$ , the parabolic (see equation 10) and hyperbolic cases,  $0 \geq \varepsilon > -1$   $F$  is monotonic increasing with  $\mu$  and there is a unique real solution of (9) for any real value of  $D$ . We also see that for small values of  $\varepsilon$  there are always solutions of  $\partial F/\partial \mu = 0$  near the points  $\mu^2 = -4$  on the imaginary axis of  $\mu$ . The existence of these singularities limits the radius of convergence and usefulness of the development of  $\mu$  as a power series in  $D$  with coefficients in  $\varepsilon$  (fixed). The attempt to express the coefficient of  $\mu^3$  in (9) as a development in series in order to evaluate the coefficient and transform the equation for solution into an ordinary cubic meets with the same difficulty.

However, let us consider  $\mu = \mu(D, \varepsilon)$  as a function of  $\varepsilon$  ( $D$  real constant) and wish to develop the solution as a Taylor's series proceeding in powers of  $\varepsilon$  with coefficients functions of  $\nu = \mu(D, 0)$ . It will be necessary to see how the matter is affected by singularities of  $\mu = \mu(D, \varepsilon)$  for  $\varepsilon$  in the complex domain in the vicinity of the solution  $\varepsilon=0, \mu=\nu$  on the real axis.

Let us write equation (20) in the form

$$\begin{aligned} \frac{1}{12} \frac{\partial F}{\partial \mu} &= 1 + \frac{1}{2} \left\{ \frac{1 - (1 - \varepsilon\mu^2)^{1/2}}{(1 - \varepsilon\mu^2)^{1/2}} \right\} + \frac{\mu^2}{4} + \frac{\mu^2}{4} \left\{ \frac{2[1 - (1 - \varepsilon\mu^2)^{1/2}]}{\varepsilon\mu^2(1 - \varepsilon\mu^2)^{1/2}} - 1 \right\} \\ &= 1 + f_1(\varepsilon\mu^2) + \frac{\mu^2}{4} + \frac{\mu^2}{4} f_2(\varepsilon\mu^2) \end{aligned}$$

Now for the points  $\varepsilon=0, \mu=\nu, 1+\mu^2/4 \neq 0$  and  $f_1(\varepsilon, \mu)=0, f_2(\varepsilon, \mu)=0$ . Then if  $m$  is the lower bound of  $|1+\mu^2/4|$  on the circle  $|\mu-\nu|=r$  about  $\mu=\nu$  it is necessarily possible to choose  $r$ , so that  $m > 0$ . It is also possible to choose  $\rho$  such that  $|\varepsilon| < \rho$  makes  $f_1(\varepsilon, \mu) + f_2(\varepsilon, \mu) < m$ . Hence by Rouché's theorem  $\partial F/\partial \mu$  has within the domains  $|\mu-\nu| < r, |\varepsilon| < \rho$  the same number of zeros as  $1+\mu^2/4$  and since  $\nu$  is a point on the real axis with no zeros in its vicinity this can be made no zeros. The radius of convergence of the series for  $\mu$  in  $\varepsilon$  thus shown to exist can be proved at least sufficient for practical needs.

Choose the circle round  $\nu$  to be

$$\mu = \nu(1 + e^{i\varphi}/5) \quad (21)$$

( $e$  here and for the rest of this paragraph is the exponential). Then the real part of  $1+\mu^2/4$

$$\begin{aligned} &= 1 + \frac{\nu^2}{4} + \frac{\nu^2}{10} \cos \varphi + \frac{\nu^2}{100} \cos 2\varphi \\ &> 1 + \frac{14}{100} \nu^2. \end{aligned}$$



On this circle  $f_1(\varepsilon\mu^2) + \frac{\mu^2}{4}f_2(\varepsilon\mu^2)$

$$= f_1(\varepsilon\mu^2) + \frac{\nu^2}{4} \left( 1 + \frac{2}{5}e^{i\varphi} + \frac{1}{25}e^{2i\varphi} \right) f_2(\varepsilon\mu^2),$$

the modulus of which

$$\leq |f_1(\varepsilon\mu^2)| + \frac{\nu^2}{4} \frac{36}{25} |f_2(\varepsilon\mu^2)|.$$

Now consider  $\varepsilon\mu^2$  as the other variable (instead of  $\varepsilon$ ). Since the coefficients of  $\varepsilon\mu^2$  in the series for  $f_1$  and  $f_2$  are positive numbers the maxima of the moduli of the functions for  $|\varepsilon\mu^2| = \rho$  occur on the positive real axis—that is for  $\varepsilon\mu^2 = \rho$ . Take  $\rho = 0.35$ , then

$$\left| \begin{array}{l} f_1 \\ f_1 + f_2 \end{array} \right| < \left| \begin{array}{l} 0.12, \\ 1 + \mu^2/4 \end{array} \right|, \quad \left| f_2 \right| < 0.38$$

whence

So that  $\partial F/\partial \mu$  has the same number of zeros in the circle (21) with  $\varepsilon\mu^2$  in the domain  $|\varepsilon\mu^2| \leq 0.35$  as has  $1 + \mu^2/4$ —that is none—and there are no singularities for the values of  $\varepsilon$  and  $\mu$  satisfying the given conditions. We shall see later that the nearly parabolic solution is not required for  $|\varepsilon^{1/2}\mu| > 0.58$ —that is  $|\varepsilon\mu^2| > 0.34$ .

The solution of (19) may now be obtained as a Taylor's series of the form

$$\mu = C_0 + C_1\varepsilon + C_2\varepsilon^2 + \dots \quad (22)$$

either by calculating the necessary differential coefficients or by equating coefficients taking  $D = 12\nu + \nu^3$ ,  $\nu$  being the solution for  $\varepsilon = 0$ . If this is done we find

$$C_0 = \nu$$

$$C_1 = -\frac{\nu^3}{1 + \nu^2/4} \left( \frac{1}{2^2 \cdot 3} + \frac{3}{2^4 \cdot 5} \nu^2 \right)$$

$$C_2 = -\frac{\nu^5}{(1 + \nu^2/4)^3} \left( \frac{1}{2^2 \cdot 3 \cdot 5} + \frac{127}{2^5 \cdot 3^2 \cdot 5 \cdot 7} \nu^2 + \frac{1}{2^4 \cdot 5 \cdot 7} \nu^4 - \frac{1}{2^9 \cdot 5^2 \cdot 7} \nu^6 \right)$$

The disadvantage of this method of solution is that even in the range of appropriateness of the nearly parabolic solution  $\nu$  may become large and the tabulation for the coefficients correspondingly extended.

The form of the equations determining the coefficients in (22) suggests another solution. The equation determining  $C_1$  is of form

$$C_1(1 + \nu^2/4) = -\nu^3 \text{ (polynomial of degree 2 in } \nu \text{)}.$$

The polynomial has no term of the first power in  $\nu$ , so that if we divide throughout by  $1 + \nu^2/4$  we can obtain a remainder of the form  $\gamma_1\nu^3$  where  $\gamma_1$  is a numerical constant, so that if we add a term  $\gamma_1\nu^3\varepsilon$  to the  $12\nu + \nu^3$  side of the original equation the coefficient of  $\varepsilon$  would become a polynomial of degree 2 and  $\gamma_1$  a constant to be determined in the process of equating coefficients. Similarly it is possible to obtain a form of coefficient avoiding fractions for the higher powers of  $\varepsilon$  by equating coefficients in a solution of the form

$$\left. \begin{aligned} D &= 12\sigma + \sigma^3\varepsilon^2 \\ &= 12\mu + \mu^3(1 + \varepsilon)6 \left( \frac{1}{2 \cdot 3} + \frac{1 \cdot 3}{2 \cdot 4} \frac{\varepsilon\mu^2}{5} + \dots \right), \\ \varepsilon^2 &= 1 + \gamma_1\varepsilon + \gamma_2\varepsilon^2 + \dots, \\ \mu &= \sigma(1 + G_1\varepsilon + G_2\varepsilon^2 + \dots), \\ \text{with } G_1 &= g_{12}\sigma^2, \\ G_2 &= g_{22}\sigma^2 + g_{24}\sigma^4, \\ &\dots \end{aligned} \right\} \quad (23)$$

where  $G_n$  is a polynomial of degree  $2n$  in  $\sigma$  an auxiliary quantity determined by the first equation. Here the first coefficients are

$$\begin{aligned} G_1 &= -\frac{3}{2^2 \cdot 5} \sigma^2, \\ G_2 &= -\frac{1}{2 \cdot 5^2 \cdot 7} \sigma^2 + \frac{1}{2^3 \cdot 5^2 \cdot 7} \sigma^4, \\ G_3 &= -\frac{13}{3^2 \cdot 5^3 \cdot 7} \sigma^2 + \frac{71}{2^3 \cdot 3^2 \cdot 5^3 \cdot 7} \sigma^4 + \frac{1}{2^4 \cdot 3^2 \cdot 5^2 \cdot 7} \sigma^6, \\ G_4 &= -\frac{107}{2^2 \cdot 3^2 \cdot 5 \cdot 7^2 \cdot 11} \sigma^2 + \frac{6679}{2^4 \cdot 3^2 \cdot 5^3 \cdot 7^2 \cdot 11} \sigma^4 + \frac{221}{2^6 \cdot 5^3 \cdot 7^2 \cdot 11} \sigma^6 + \frac{43}{2^8 \cdot 5^3 \cdot 7^2 \cdot 11} \sigma^8, \\ G_5 &= -\frac{2^9 \cdot 103}{3 \cdot 5^5 \cdot 7^2 \cdot 11 \cdot 13} \sigma^2 + \frac{214601}{2^4 \cdot 3^2 \cdot 5^5 \cdot 7 \cdot 11 \cdot 13} \sigma^4 + \frac{178849}{2^6 \cdot 3^2 \cdot 5^5 \cdot 7^2 \cdot 11 \cdot 13} \sigma^6 \\ &\quad + \frac{123791}{2^8 \cdot 3^2 \cdot 5^5 \cdot 7^2 \cdot 11 \cdot 13} \sigma^8 + \frac{1213}{2^8 \cdot 3^2 \cdot 5^5 \cdot 7 \cdot 11 \cdot 13} \sigma^{10}, \\ c^2 &= 1 - \frac{4}{5} \epsilon - \frac{6}{5^2 \cdot 7} \epsilon^2 - \frac{52}{3 \cdot 5^3 \cdot 7} \epsilon^3 - \frac{107}{3 \cdot 5 \cdot 7^2 \cdot 11} \epsilon^4 - \frac{2^{11} \cdot 103}{5^5 \cdot 7^2 \cdot 11 \cdot 13} \epsilon^5 \dots, \end{aligned}$$

where the exponent is placed on  $c$  so that the first equation can be conveniently written in the same form as that for the parabola and solved by the use of the same table. The extreme value of  $\epsilon$  for which the nearly parabolic solution is necessary is 0.07, for which the first neglected term of  $c^2$  is  $0.8 \times 10^{-9}$ .

In the process leading to the previous solution it would have been possible to carry on the division by  $(1 + v^2/4)$  a step further to give a remainder of the form  $\beta_1 v$  and destroyed the fractional form of the  $C_1$  term in the solution in Taylor's series by adding a term  $\beta_1 v \epsilon$  to the left-hand member of the equation determining the coefficients. This suggests a solution of the form

$$12\tau + \tau^3 b = 12\mu + \mu^3(1 + \epsilon)6 \left( \frac{1}{2 \cdot 3} + \frac{1 \cdot 3}{2 \cdot 4} \frac{\epsilon \mu^2}{5} + \dots \right),$$

with

$$\begin{aligned} b &= 1 + \beta_1 \epsilon + \beta_2 \epsilon^2 + \dots, \\ \mu &= \tau(1 + H_1 \epsilon + H_2 \epsilon^2 + \dots), \end{aligned}$$

where  $H_n$  is a polynomial of degree  $2n$  in  $\tau$ . The first terms of this solution are given by

$$\begin{aligned} H_1 &= \frac{4}{3 \cdot 5} - \frac{3}{2^2 \cdot 5} \tau^2, \\ H_2 &= \frac{242}{3^2 \cdot 5^2 \cdot 7} - \frac{43}{2 \cdot 5^2 \cdot 7} \tau^2 + \frac{1}{2^3 \cdot 5^2 \cdot 7} \tau^4, \\ &\dots \dots \dots \\ b &= 1 + \frac{4}{3 \cdot 5} \epsilon + \frac{242}{3^2 \cdot 5^2 \cdot 7} \epsilon^2 + \dots \end{aligned}$$

It is a pleasure to acknowledge the helpful conversations I had with Mr. W. B. Smith-White, who kindly read a draft of this section before it was offered as a contribution to him in his capacity of editor.

## NUMERICAL CONSIDERATIONS.

Kepler's equation may for purposes of calculation be written in a number of ways according to the tastes of the computer or the tables he has available; among these are

$$\begin{aligned}[M] + \{e\}(\sin E) &= E \\ -\left[\frac{M}{e}\right] + \left\{\frac{1}{e}\right\}(E) &= \sin E \\ [M] + \{e\}(Y) &= \sin^{-1} Y \\ [M] - \{1-e\}(Y) &= \sin^{-1} Y - Y\end{aligned}$$

where  $\sin E = Y$ . The quantity in the square bracket is put into the product register of the calculating machine, that in the curly bracket in the setting register and the quantity in the plain bracket built up in the multiplier register till the right-hand member of the equation appearing in the product register has the value corresponding to that in the plain bracket. The first two forms, due to Comrie and Strömgren respectively (see Möller, 1933), require a table of sines with argument in decimals of a degree or in radians. The recently published Chambers Six-Figure Mathematical Tables (Comrie, 1949) are most suitable. Reasonably near to perihelion the third and fourth forms are useful. The tables of Möller (1940) and Strömgren (1945) are particularly suitable for the last form, which is valuable in the range of values, to be discussed shortly, when computation with an extra figure is necessary. The last three forms have the advantage that the quantity to appear in the multiplier register, being the argument of the mathematical table, can be more conveniently built up to its full number of tabulated figures. It should be added that the second method can be used even if  $e$  is small, since although its reciprocal is large and the significant figures of  $E/e$  and  $M/e$  are moved relative to those  $\sin E$  the same thing occurs with the equation in its original form and indeed (if only  $E$  were required) for a five-figure solution of  $M = E - e \sin E$  with  $e < 0.1$  the value of  $\sin E$  would be needed to only four decimals.

If the tables for  $\sin E$  extend only to  $\pi/2$  the equation may be used past this point in the form

$$(\pi - M) - e \sin(\pi - E) = \pi - E$$

or

$$\frac{\pi - M}{e} - \frac{\pi - E}{e} = \sin(\pi - E)$$

It is well known that the accuracy of solution of Kepler's equation falls off when  $e$  tends towards 1. Suppose equation (7) has been solved by using a table of sines. Let the solution obtained be  $E_1$ ,  $\sin_t E_1$  the value of its sine simultaneously obtained from the table and  $E$  the accurate solution.

Then

$$M = E_1 - e \sin_t E_1,$$

$$\sin_t E_1 = \sin E_1 + \Delta,$$

$$E_1 = E + \delta E,$$

and

$$\sin_t E_1 = \sin E + \delta \sin E$$

where the last three equations are definitions of  $\Delta$ , the error of the table and of  $\delta E$  and  $\delta \sin E$ , the errors in the solutions for  $E$  and  $\sin E$  respectively. From these equations with (7)

$$\delta E = \frac{e \Delta}{1 - e \cos E} \quad \text{and} \quad \delta \sin E = \frac{\Delta}{1 - e \cos E}$$

If we are working with a table to  $n$  figures the maximum error (now called  $\Delta$ ) of the table will be  $0.5 \times 10^{-n}$  and its average value would be half of this.

The rectangular coordinates in the plane of the orbit are

$$\begin{aligned}x_0 &= a (\cos E - e) \\ y_0 &= a(1 - e^2)^{1/2} \sin E\end{aligned}$$

and the maximum errors in these arising from errors in solving Kepler's equation and (another  $\Delta$ ) in extracting  $\cos E$  from the tables are

$$\begin{aligned}\delta x_0 &= a \Delta (e \sin E + 1 - e \cos E) / (1 - e \cos E) \\ \delta y_0 &= a(1 - e^2)^{1/2} \Delta / (1 - e \cos E)\end{aligned}$$

The effect that these errors has on the position of a body on the celestial sphere depends on their relation in direction and magnitude to the geocentric distance vector, but as this relation differs for every body and for the same one at different times it is best for the purpose of establishing a measure of the influence of the errors on the position of an object to compare their magnitude with that of the heliocentric distance,  $r$ . Now

$$r = a(1 - e \cos E)$$

so that using the relations above

$$\frac{\{(\delta x_0)^2 + (\delta y_0)^2\}^{1/2}}{r} = \frac{(2 + 2e \sin E)^{1/2}}{(1 - e \cos E)^{3/2}} \Delta \quad (24)$$

The value of the coefficient of  $\Delta$  in (24) which may be tolerated is arbitrary, but 3 seems a reasonable figure and one which will not introduce errors from this cause more serious than must be admitted in almost any extended calculation. If the values of  $M$  and  $e$  are plotted as abscissa and ordinate on a plane, the curve given by (7) and

$$\frac{(2 + 2e \sin E)^{1/2}}{(1 - e \cos E)^{3/2}} = 3$$

defines the boundary of the region in which Kepler's equation will give a satisfactory result. Beyond this region is an area in which it is profitable if we want a result accurate to  $n$  figures to work with a table to  $n+1$  decimals. The boundary of this region is given by

$$\frac{(2 + 2e \sin E)^{1/2}}{(1 - e \cos E)^{3/2}} = 30$$

and beyond this methods adapted for nearly parabolic solutions should be used. Also consider the equation

$$x_0 = a(\cos E - e)$$

and suppose the possible error in the tabulation of  $\cos E$  to be  $\Delta_1$ , then

$$\delta x_0 / r = \Delta_1 / (1 - e \cos E) \quad (25)$$

along the extra figure boundary  $(1 - e \cos E)^{-1}$  has values from 1.8 to 2.5 and along the nearly parabolic boundary from 7.8 to 8.5, which shows that it is necessary to work with the extra figure, when it is appropriate, even after the determination of  $E$  (or  $\sin E$ ). For small geocentric distances, say less than 0.3 astronomical unit, it would be necessary to use the extra figure apart from the considerations arising above.

If we work through the case of the hyperbolic orbit, equation (8), in the same way as has been done for the ellipse we find the boundary beyond which extra figure computation is necessary is given by

$$\frac{(2e \cosh F + 2e \sinh F)^{1/2}}{(e \cosh F - 1)^{3/2}} = 3$$

and that beyond which nearly parabolic solution must be used by

$$\frac{(2e \cosh F + 2e \sinh F)^{1/2}}{(e \cosh F - 1)^{3/2}} = 30$$

Both equations are taken with equation (8) if  $M$  is to be plotted against  $e$ .

Figure 2 shows these curves which define the regions in which the various types of computation are appropriate. In Figure 3 the area in which nearly parabolic solution is desirable is represented on the plane of  $e$  and  $\sin E (= \epsilon^{1/2} \mu)$   $M$  and  $\sin E$  are always available when calculating in the ordinary way or with

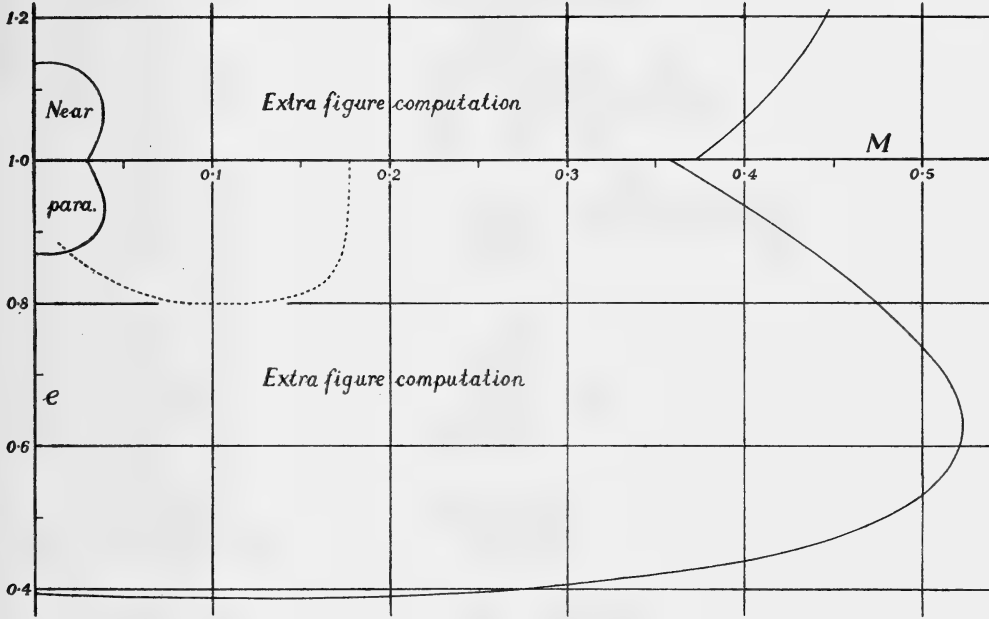


Fig. 2.—Method of solution according to values of  $e$  and  $M$ .

the extra figure and a quantity approximating to  $\epsilon^{1/2} \mu$  is available at a stage in the nearly parabolic solution which I hope to publish soon so that these diagrams facilitate a decision as to which type of computation is to be used, or in some cases when a change of process is necessary. In doubtful cases either of the possible alternatives should be satisfactory. It may be pointed out that the nearly parabolic solution is not necessary except when  $\sin E < 0.53$  or  $\sinh F < 0.58$  and by the previous discussion the development in series of the solution for the co-ordinate  $\mu$  is then permissible.

Many transformations of Kepler's equation have been used to provide solutions, ones of importance being by Tietjen (see Bauschinger, 1934), Howe (see Plummer, 1919) and Oppolzer and Marth (see Marth, 1890b). Oppolzer and Marth, independently, wrote the equation in the form

$$\tan (E-M) = \frac{e \sin M}{\lambda - e \cos M},$$

where

$$\lambda = \frac{E-M}{\sin (E-M)}.$$

Tables for this solution were given by the two authors mentioned and more recently Subbotin (1929) has used it tabulating  $\log \lambda$  to seven decimal places

with argument  $\tan (E-M)$ . It is of interest to examine the range of applicability of this transformation of Kepler's equation as was done for the equation itself in the previous paragraphs.

We obtain

$$\begin{aligned}\delta E &= \frac{\tan (E-M)}{\sec^2 (E-M) \{ \cos (E-M) + (E-M) \sin (E-M) - e \cos M \}} \Delta \\ &= \frac{\frac{1}{2} \sin 2 (E-M)}{\cos (E-M) + (E-M) \sin (E-M) - e \cos M} \Delta\end{aligned}$$

Where  $\Delta$  is the error of the tabulated value of  $\lambda$ . The ratio of the error arising from  $\delta E$  in the position of the body on the plane of its orbit to the radius vector

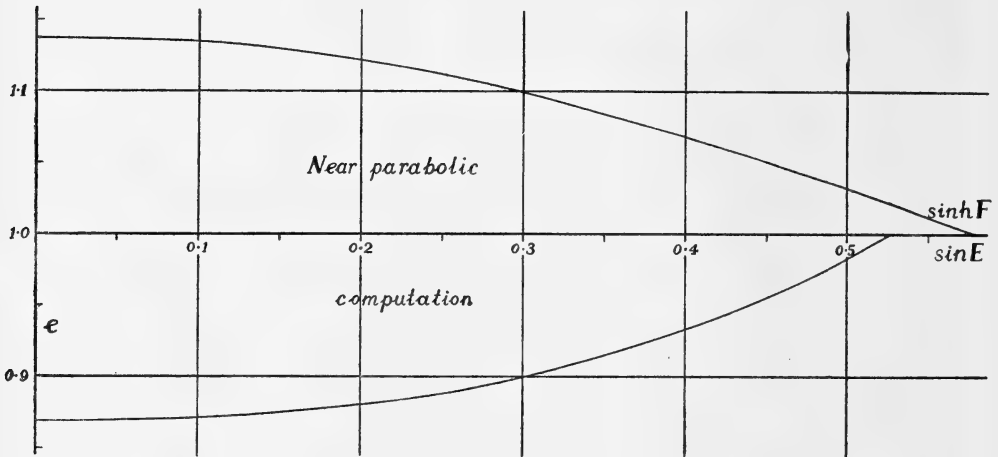


Fig. 3.—Method of solution according to values of  $e$  and  $\sin E$  (or  $\sinh F$ ).

is

$$\begin{aligned}\frac{\{(\delta x_0)^2 + (\delta y_0)^2\}^{1/2}}{r} &= \left\{ \frac{1+e \cos E}{1-e \cos E} \right\}^{1/2} \delta E \\ &= \left( \frac{1+e \cos E}{1-e \cos E} \right)^{1/2} \frac{\frac{1}{2} \sin 2 (E-M)}{\cos (E-M) + (E-M) \sin (E-M) - e \cos M} \Delta\end{aligned}\quad (26)$$

If we are prepared to allow the coefficient of  $\Delta$  in this equation to attain the value 3 and as before map the boundary of the area for which the transformation is applicable, we are applying a rather less severe test since the error in the equation includes the effect arising only from the error in calculating  $E$  and neglects errors in the tables subsequently used for computing  $x_0$  and  $y_0$ . Nevertheless, the boundary which is shown by the dotted curve on Figure 2 indicates that while the method of solution does represent an improvement on that using a table of sines to the same number of figures, it does not improve on the accuracy obtained by using the sine table to an extra figure nor encroach appreciably on the area in which a nearly parabolic solution is needed.

It is thus not possible to dispense with extra figure calculation unless we are willing to extend unduly the tabulation for nearly parabolic solutions. Equations (25) and (26) show that however accurately  $E$  may be determined the solution in terms of eccentric anomaly leads to difficulties when  $e$  is nearly 1 and  $E$  is small.

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The following bibliography is supplementary to the references given by Radau (1900), Bauschinger (1901 and 1934), Herglotz (1906) and Wintner (1941). Material listed by these authors has not been repeated unless referred to in my article. The titles of the references do not always show satisfactorily the aspect of Kepler's Problem with which they deal, so they are omitted and the contents indicated by a code, which has the further advantage of economy.

- G, indicates a general account such as might be given by a text book, a review article or an article chiefly didactic in purpose,
- T, that the main interest is theoretical,
- S, an article whose main purpose is to describe or discuss a method of obtaining a solution of Kepler's Problem, and
- I, a solution depending on numerical integration or the application of finite differences.
- e, indicates that the article refers to elliptic motion,
- n, to nearly parabolic motion, and
- p, to parabolic motion.
- s, indicates a solution in power series,
- f, a solution in trigonometric series,
- g, that the solution is graphical or mechanical and
- c, that a numerical solution is given (c is only used if two methods are described otherwise solutions may be assumed to involve numerical methods),
- t, indicates that tables are given to aid the purpose of the article and
- z, that I have not seen the article myself and depend on a review or abstract for its description.

This bibliography is meant to be fairly comprehensive for categories S and T. Developments whose main application lies in the study of perturbed motion have usually been omitted except for some borderline cases under the heading I. The historical aspect has been neglected entirely but those who are interested will find valuable guidance in Radau (1900), Herglotz (1906) and Wintner (1941); and the bibliography of Houzeau and Lancaster (1887, 1889) gives many references, nearly all of which were inaccessible to me. The collected works of Kepler have been edited by Frisch (1858-71) and a recent account of "de motibus stellae Martis" is given by Pannekoek (1948).

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# A NEW METHOD OF MEASUREMENT OF THE SURFACE TENSION OF VISCOUS LIQUIDS.

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## INTRODUCTION.

The measurement of the surface tension of viscous liquids, such as molasses, by usual methods, is often hindered by factors arising from the high viscosity of the liquid. Thus L'eaute (1935) in measuring the surface tension of tars and bitumen by capillary rise, notes that equilibrium condition for bitumen is reached in 360 hours. In the Sugden bubble pressure method, the time required to blow the bubble with no viscosity interference is of the order of ten minutes, an unpracticably long time. With the Du Nouy tensiometer, the break point for molasses is poorly defined.

The method now presented is a development of the Eötvös reflection method for sessile drops and is independent of viscosity. It may be applied to the measurement of the surface tension of liquids in general, with particular value for viscous liquids such as molasses and other concentrated sugar syrups.

Previous methods of measuring surface tension from the shape of sessile drops have relied on actual measurement of radii of curvature and other drop dimensions, usually made on the profile of the drop. Thus Worthington (1881) projected the form of *hanging* drops of water on a screen and measured radii of curvature and the volume of the drop. His work was amplified by Ferguson (1912), who photographed the drop. Moser (1927) calculated surface tensions from observations made vertically on sessile drops, and proposed refinements of the original method used by Eötvös (1886). Moser's observations were made with a telescope, to measure the vertical distance between two points of reflection on the curved surface of the drop and also the angles at which the light was reflected. Kemball (1946) employed side view illumination and a comparator for measuring sessile drops of mercury, and calculated the surface tension from the height and equatorial diameter of the drop. Taylor and Alexander (1944) also used side view illumination. They photographed sessile drops formed on the end of a brass tube and, from the photograph, measured the height of the drop above its equatorial plane, the equatorial diameter and thence calculated the surface tension.

## EXPERIMENTAL.

In the method now presented, a drop of liquid on a plane surface (not wetted by the liquid) is illumined from above by two point sources of light, and photographed by a camera placed between the lights. A millimetre scale is also included in the photograph, which shows the images of the lights reflected by the drop. The distance between these images is measured by reference to the photographed millimetre scale. The equatorial diameter of the drop is also measured from the photograph. The distance from the light to the drop, and the distance between the lights are also measured. Figure 1, which is not

drawn to scale, illustrates the method of deriving the radius of curvature of the drop from these measurements.

From a consideration of the similar triangles  $L_1L_2F$  and  $I_1I_2F$ , we get

$$\frac{a}{x} = \frac{y}{\text{focal length}}$$

$$= \frac{y}{\frac{1}{2}b}$$

$$\text{Then } b = \frac{2xy}{a} \dots\dots\dots (1)$$

where  $b$  = the radius of curvature at the vertex of the drop.

$x$  = the distance of the drop from the light.

$y$  = the distance between the images on the drop.

$a$  = the distance between the lights.

$x$  and  $a$  are large in comparison with  $b$  and  $y$ . In the actual apparatus  $x$  was 68 cm.,  $a$  was 47 cm., while  $b$  and  $y$  were usually of the order of 0.3 cm.

The value of  $b$  thus found, together with  $r$ , the equatorial radius of the drop (measured from the photograph) is then used to calculate the surface tension by means of a formula,

$$\text{Surface tension} = \gamma = \frac{r^3}{b-r} \times \frac{dg}{6} \text{ dynes cm.}^{-1}.$$

where  $d$  = density difference between liquid and surrounding gas, in gm. cm.<sup>-3</sup>.

$g$  = gravitational acceleration in cm. sec.<sup>-2</sup>.

#### DEDUCTION OF THE FORMULA.

The formula above was obtained from a study of the tables of Bashforth and Adams (1883). These tables give the values of  $b/x$  at a series of values of a dimensionless quantity, defined as

$$\beta = \frac{gdb^2}{\gamma}$$

where  $b$  is the radius of curvature at the vertex of the drop and  $\gamma$  is the surface tension.

$x$  is the horizontal distance from the surface of the drop to its axis. The maximum value of  $x$  we have designated as  $r$  and thus obtained values of  $b/r$  as an empirical function of  $\beta$ . Empirically it has been found that there is an

almost linear relationship between  $\beta$  and  $\frac{b^2}{r^2} \left( \frac{b}{r} - 1 \right)$  and the ratio  $\frac{\beta}{\frac{b^2}{r^2} \left( \frac{b}{r} - 1 \right)}$

has an almost constant value of 6.0 over the range  $0 < \beta < 4$ . This ratio  $\frac{\beta}{\frac{b^2}{r^2} \left( \frac{b}{r} - 1 \right)}$

cancels to  $\frac{r^3}{b-r} \frac{dg}{\gamma}$  which we will designate as  $\alpha$ . Values of  $\beta$ ,  $\frac{b^2}{r^2} \left( \frac{b}{r} - 1 \right)$  and

this quotient  $\alpha$  are given in Table I.

TABLE I.  
*Values of the Dimensionless Quantities Concerned with the Shape of Drops Calculated from the Tables of Bashforth and Adams.*

$\beta = \frac{gdb^2}{\gamma}$	$\frac{b^2}{r^2} \frac{b}{r} - 1$	$\alpha = \left( \frac{r_3}{b-r} \frac{dg}{\gamma} \right)$
0.1	0.01656	6.037
0.2	0.03316	6.031
0.3	0.049735	6.032
0.4	0.06626	6.036
0.5	0.08275	6.042
0.6	0.099245	6.045
0.7	0.115755	6.047
0.8	0.13226	6.049
0.9	0.14879	6.049
1.0	0.16533	6.049
1.2	0.19845	6.047
1.4	0.231675	6.043
1.6	0.26497	6.038
1.8	0.29836	6.033
2.0	0.331845	6.027
2.2	0.36543	6.020
2.4	0.29910	6.013
2.6	0.43290	6.006
2.8	0.46675	5.999
3.0	0.50073	5.991
4.0	0.67207	5.952
5.0	0.84569	5.912
6.0	1.0214	5.874
7.0	1.1991	5.837
8.0	1.3787	5.802
9.0	1.56015	5.768
10.0	1.7431	5.737
15.0	2.68035	5.596
20.0	3.6494	5.480

It will be seen that for the range  $\beta=0.1$  to  $\beta=4.0$  the proportionality factor is  $6.00 \pm 1$  per cent. maximum variation.

Thus

$$\frac{r^3}{b-r} \frac{dg}{\gamma} = 6.0$$

or

$$\gamma = \frac{r^3}{b-r} \frac{dg}{6.0} \dots\dots\dots (2)$$

where  $\gamma$  = the surface tension in dynes cm.<sup>-1</sup>.

$r$  = the equatorial radius of the drop in cm.

$b$  = the radius of curvature at the vertex of the drop in cm.

$g$  = the gravitational acceleration in cm. sec.<sup>-1</sup>.

$d$  = density difference between liquid and surrounding gas in gm. cm.<sup>-3</sup>.

This equation used in conjunction with (1) provides an easy method of determining the surface tension from the measurement of the images reflected in sessile droplets.

#### *Maximum Size of Drops.*

In using the equation

$$\gamma = \frac{r^3}{b-r} \frac{dg}{6.0}$$

It is necessary for the drops to conform to the requirement that  $\beta$  be not greater than 4.0. This is evident from Table I, and therefore places an upper limit on the size of the drop. This maximum size can be deduced in the following manner :

The upper limit of the size of the drop depends on the surface tension and the density of the liquid under investigation.

Taking as the limiting condition

$$\beta = 4.0$$

i.e. 
$$g \frac{db^2}{\gamma} = 4.0$$

this gives the limiting value of  $b$  as

$$b = \sqrt{\frac{4\gamma}{gd}}$$

Substituting this value of  $b$  in equation (2), we get

$$2 \sqrt{\frac{\gamma}{gd} - r} \frac{r^3}{\gamma} = 6.0$$

whence 
$$gdr^3 + 68r - 12 \sqrt{\frac{\gamma^3}{gd}} = 0 \dots\dots\dots (3)$$

This is an expression for the limiting radius ( $r$ ) of the droplet.

On substituting the approximate values for the density and surface tension of the liquid concerned, this equation may be solved numerically to give the maximum value of  $r$ .

Thus, for one of the more viscous liquids which it is proposed should be examined by this method, namely molasses, we have approximately

$$d = 1.4 \text{ gm. cm.}^{-3}$$

$$\gamma = 65 \text{ dynes cm.}^{-1}.$$

Substituting these values in equation (3), we get

$$1372r^3 + 390r - 169.6 = 0$$

or 
$$r = 0.320 \text{ cm.}$$

This means that the approximation implicit in equation (2) may be used with molasses for all drops up to a limiting diameter of 6.4 mm. This is quite a reasonably large drop.

For ethyl alcohol, a liquid with a low specific cohesion, we have

$$d = 0.8 \text{ gm. cm.}^{-3}$$

$$\gamma = 22 \text{ dynes cm.}^{-1}.$$

Substituting these values in (3) and solving for  $r$  as above, we obtain

$$r = 0.246 \text{ cm.}$$

Thus the maximum diameter of a drop of ethyl alcohol to be tested by this method is 0.49 cm.

Taking mercury as an example of a liquid with high surface tension, we have

$$d = 13.6 \text{ gm. cm.}^{-3}$$

$$\gamma = 488 \text{ dynes cm.}^{-1}$$

from which the maximum value of  $r$  is  $r = 0.281 \text{ cm.}$ , whence the maximum diameter is 0.56 cm.

In all cases examined it seems that the proposed method can be used over a reasonable range of drop diameter.

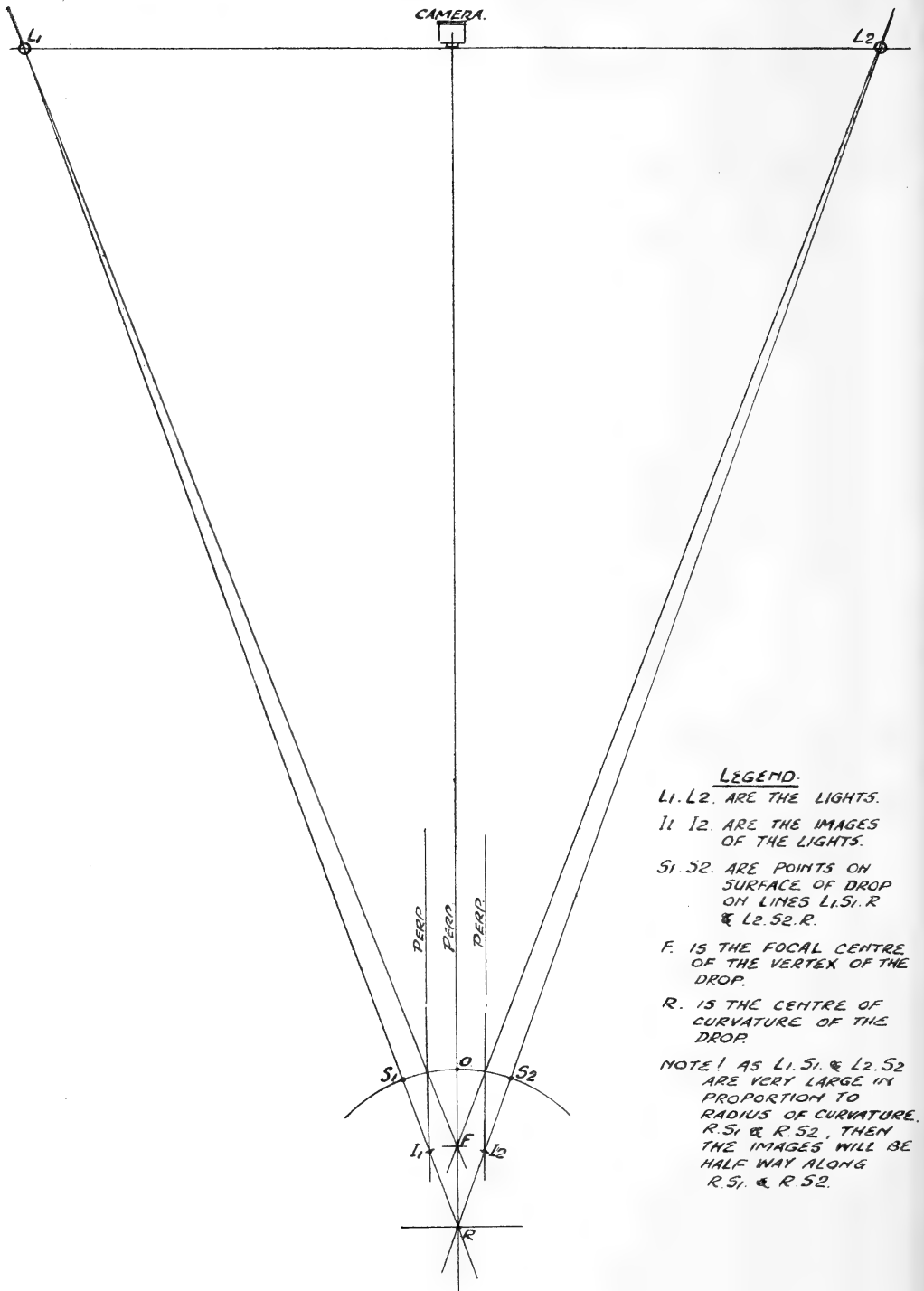


Fig. 1.

## DISCUSSION.

The method proposed for the measurement of surface tension involves the measurement on a sessile drop, of the equatorial radius ( $r$ ) and the radius of curvature at the vertex ( $b$ ). It has been shown that these two quantities are related to the surface tension ( $\gamma$ ), and the density of the liquid by the simple approximate formula

$$\gamma = \frac{r^3}{b-r} \frac{dg}{6}$$

This equation holds with an accuracy of 1 per cent. for all droplets below a certain limiting size. This limiting size depends on specific cohesion of the liquid concerned.

The method is particularly valuable for viscous liquids, since, being essentially a static method, it avoids errors arising from the slow attainment of equilibrium in such more familiar methods as the drop weight, ring, capillary rise and bubble pressure methods.

The experimental method is outlined in this paper and consists essentially of photographing a droplet of the liquid, illumined by two point sources of light. The results obtained from the examination of a number of standard liquids, by this method, will be presented in a later paper.

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## THE CHEMISTRY OF RUTHENIUM.

### PART VI. THE EXISTENCE OF THE TRIS-O-PHENANTHROLINE RUTHENIUM II AND TRIS-O-PHENANTHROLINE RUTHENIUM III IONS IN ENANTIOMORPHOUS FORMS.

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*Manuscript received, September 8, 1949. Read, October 5, 1949.*

The resolution of tris 2:2' dipyridylruthenium II bromide into optical forms of great stability was achieved by Burstall (1936), through the tartrate, thus demonstrating the octahedral distribution of the groups about hexacovalent bivalent ruthenium. Recently, the analogous tris o-phenanthroline compounds,  $\text{Ru}(\text{phenan})_3\text{X}_2$ , were isolated (Dwyer, Humpoletz and Nyholm, 1946), but although the complexes were of great stability, and obviously of similar composition to the dipyridyl compounds, attempts at resolution through the tartrate, acid tartrate, bromcamphorsulphonate, and camphorsulphonate failed. In this paper the resolution of the tris o-phenanthroline complexes, through the antimonyl tartrate, is described.

When a solution of potassium antimonyl tartrate was added to a solution of tris o-phenanthroline ruthenium II chloride an orange crystalline precipitate resulted. This was found to be the almost pure d, tris-o-phenanthroline ruthenium II antimonyl tartrate, whilst the residual solution was strongly laevo rotatory. The conditions of precipitation were not critical, since the antimonyl tartrate of the d form appeared to be very insoluble, whilst the antimonyl tartrate of the l form was very soluble. Addition of a very large excess of potassium antimonyl tartrate failed to precipitate the laevo form. The crystalline d form was too insoluble in water to be crystallised easily, but was purified by solution in dilute alkali, followed by reprecipitation with acetic acid. The optically active acid radicle was eliminated from the purified material by solution in alkali and precipitation of either the perchlorate or iodide by the addition of sodium perchlorate or potassium iodide. These salts could be crystallised from water, but the perchlorate was the more suitable from the point of view of solubility. The perchlorate of the laevo form was obtained from the original laevo chloride solution by the addition of sodium perchlorate, and crystallised several times from warm water.

The optical forms were notably stable and could be crystallised repeatedly from hot water or alcohol, dissolved in six normal sulphuric acid or kept in aqueous solution at room temperature for over two months without change of rotation. The specific rotations of the forms were as follows:  $[\alpha]_{\text{D}}^{20} = +1340^\circ$  and  $-1328^\circ$ ; and  $[\alpha]_{5461}^{20} = +2559^\circ$  and  $-2550^\circ$ . It is thus evident that the substance has a very large abnormal rotatory dispersion, and probably, when the complete rotatory dispersion curve is obtained, an anomalous rotatory dispersion. Burstall found  $[\alpha]_{5791}^{25} = +860^\circ$  and  $-815^\circ$  for the dipyridyl compound. It is probable that this substance too possesses an abnormal rotatory dispersion.



The optical forms were oxidisable with ceric nitrate to the blue ruthenium III complex, which was unstable except in high concentrations of acid (Dwyer, Humpoletz and Nyholm, 1946). The potential of the reaction  $\text{Ru(phenan)}^{++}$  d or l form  $\rightarrow \text{Ru(phenan)}^{+++}$  in six normal sulphuric acid at  $0^\circ \text{C}$ . was found to be  $1.17 \text{ volts} \pm 0.003 \text{ volt}$ . The same value was obtained from the racemate by determining the potential with a mixture of the two optical forms. (See also Dwyer, 1949.) This is the first occasion that the redox potential of an enantiomorphous form has been compared with the racemate. It is unfortunate that the instability of the system precluded a more accurate value of the potentials.

When d or l tris-o-phenanthroline ruthenium II perchlorate in six normal sulphuric acid was oxidised with ceric nitrate the resulting blue solution containing the tris-o-phenanthroline ruthenium III ion was found to be optically active, but the rotation was different. The activity was lost rapidly at  $20^\circ \text{C}$ ., but if the solution was immediately reduced with ferrous sulphate, the active ruthenium II compound was regenerated with its rotation unchanged. Since the ruthenium III complex could not be isolated the specific rotation has been calculated for the ion  $\text{Ru(phenan)}_3^{+++}$ . For comparison the rotation of the ion  $\text{Ru(phenan)}_3^{++}$  are also calculated.\*

Ion.	N <sub>AD</sub> .	Hg <sub>5461</sub> .
d $\text{Ru(phenan)}_3^{++}$ .. ..	+1834°	+3494°
l $\text{Ru(phenan)}_3^{++}$ .. ..	—1818°	—3482°
d $\text{Ru(phenan)}_3^{+++}$ .. ..	+584°	+2330°
l $\text{Ru(phenan)}_3^{+++}$ .. ..	—568°	—2354°

It is evident that the ion  $\text{Ru(phenan)}_3^{+++}$  also has an abnormal rotatory dispersion. The resolution of hexavalent ruthenium III complexes has already been carried out by Werner and Smirnoff (1920) and Charonnat (1931). The present observations are of particular interest, however, in that they provide a unique demonstration of the similarity of the oxidised and reduced forms of the o-phenanthroline complex, as well as of the essential simplicity of the oxidation/reduction reaction.

Preliminary experiments with the d form of the dipyriddy complex ion  $\text{Ru(dipy)}_3^{++}$  show that this is also oxidisable with persistence of the optical activity, but the sign of the rotation is changed on oxidation. The results of the experiments on this compound, the resolution of the nickel and ferrous tris-o-phenanthroline complexes, and the complete rotatory dispersion curves for a number of such complexes will be published in subsequent communications.

#### EXPERIMENTAL.

(A 2 dm. tube was used for all determinations of the rotation.)

##### *d-Tris-(o-Phenanthroline)-Ruthenium II d-Antimonyl Tartrate Dihydrate.*

Tris-o-phenanthroline ruthenium II iodide (Dwyer, Humpoletz and Nyholm, 1946), 1.3 g., was dissolved in 100 mls. of hot water, and excess of silver chloride added. The mixture was shaken for five to ten minutes to transform the iodide to the chloride, and filtered with the addition

\* In making the transformation from the specific rotations of the salts to the specific rotations of the ions in the preliminary note to *Nature*, 163, 918 (1949) an error was made in the calculations.

of filter paper pulp. Potassium antimonyl tartrate (0.5 g.) in 30 mls. of water was added slowly to the cold chloride, with scratching. The voluminous orange-yellow precipitate was washed several times with water and dissolved with shaking in 75 mls. of cold N/20 sodium hydroxide. Dilute acetic acid was then added until acid, and a small volume of potassium antimonyl tartrate solution, when the substance reprecipitated as orange prismatic needles. It was insoluble in alcohol and sparingly soluble in water, but dissolved easily in the presence of a trace of alkali.

A 0.02% solution in M/100 NaOH gave  $\alpha = +0.30^\circ$ , whence  $[\alpha]_D^{20} = +750^\circ$ .

Found: N=6.84%; Sb=19.45%.

Calculated for  $[\text{Ru}(\text{Cl}_{12}\text{H}_8\text{N}_2)_3][\text{SbO}_2\cdot\text{C}_4\text{H}_4\text{O}_6]\cdot 2\text{H}_2\text{O}$ : N=6.82%; Sb=19.48%.

*d-Tris-(o-Phenanthroline) Ruthenium II Perchlorate Monohydrate.*

The d-antimonyl tartrate (0.6 g.) was dissolved in N/20 caustic soda (50 mls.) and the solution filtered. Sodium perchlorate solution (3 N approx.) was added slowly in excess, and the resulting orange-yellow precipitate filtered and washed with ice water containing a little perchloric acid. It was finally crystallised twice from warm water containing a trace of perchloric acid. Alternatively it could be crystallised from warm methanol by the addition of ether. The substance gave micro prismatic needles, which were easily soluble in warm water and alcohol. It was much more soluble than the perchlorate of the racemate.

A 0.205% solution in water gave  $\alpha_D = +0.55^\circ$  and  $\alpha_{5461} = +1.05^\circ$ ; whence  $[\alpha]_D^{20} = +1340^\circ$  and  $[\alpha]_{5461}^{20} = +2560^\circ$ .

Found: Ru=11.7%; N=9.87%.

Calculated for  $[\text{Ru}(\text{C}_{12}\text{H}_8\text{N}_2)_3][(\text{ClO}_4)_2\cdot\text{H}_2\text{O}]$ : Ru=11.8%; N=9.78%.

*l-Tris-(o-Phenanthroline) Ruthenium II Perchlorate Monohydrate.*

The original solution left after addition of potassium antimonyl tartrate contained approximately half of the substance taken, and was strongly laevo. It was treated with a further portion of antimonyl tartrate solution containing 0.4 g. and cooled in ice to remove traces of the d form. After filtration, the solution was treated with sodium perchlorate solution, and the resulting orange-yellow precipitate of the active perchlorate crystallised twice from warm water containing a trace of perchloric acid. The substance crystallised in orange-yellow micro prismatic needles.

A 0.0211% solution in water gave  $\alpha_D = -0.56^\circ$  and  $\alpha_{5461} = -1.08^\circ$ ; whence  $[\alpha]_D^{20} = -1328^\circ$  and  $[\alpha]_{5461}^{20} = -2557^\circ$ .

Found: Ru=11.9%; N=9.65%.

Calculated for  $[\text{Ru}(\text{C}_{12}\text{H}_8\text{N}_2)_3][(\text{ClO}_4)_2\cdot\text{H}_2\text{O}]$ : Ru=11.8%; N=9.78%.

*The Redox Potentials of the d and l Forms and the Racemate.*

Approximately M/800 solutions of the two optical forms as the perchlorates dissolved in sulphuric acid 6 N were placed in a redox assembly (Dwyer, 1949) and cooled to  $0^\circ\text{C}$ . Half of the theoretical amount of ceric nitrate solution necessary for the oxidation to the ruthenium III complex was added, and the maximum potential determined. For the potential of the racemate equal volumes of the d and l forms were mixed and treated as before with ceric nitrate.

d form :  $E = 0.936\text{ v.}$ ;  $E_h = 1.169\text{ v.}$

l form :  $E = 0.933\text{ v.}$ ;  $E_h = 1.166\text{ v.}$

Racemate :  $E = 0.934\text{ v.}$ ;  $E_h = 1.167\text{ v.}$

Previous work on this system (Dwyer, Humpoletz and Nyholm, 1946; Dwyer, 1949) has shown that the potential is not reproducible to more than about 5 mv., so that it can be assumed that the potentials of the optical forms and the racemate are the same within the limits imposed by the instability of the system.

*The Persistence of Optical Activity of the Complex Cation after Oxidation.*

The d and l perchlorates in sulphuric acid 6 N were treated with drops of ceric nitrate (approx. 0.1 N in 1 N nitric acid) until the colour changed to blue. The amounts of oxidising agent needed were so small that the concentration change was neglected. The oxidised solution was immediately tested for optical activity, which was found to be still present, but the angle of rotation was smaller. A crystal of ferrous sulphate then added to each regenerated the complex ruthenium II cation, and the rotation rose to the original value.

A 0.0082% solution of the d perchlorate after oxidation gave  $\alpha_D = +0.07^\circ$  and  $\alpha_{5461} = +0.28^\circ$ ; whence the specific rotation of the d form of the ion  $\text{Ru(phenan)}_3^{+++}$   $[\alpha]_D^{20} = +584^\circ$  and  $[\alpha]_{5461}^{20} = +2330^\circ$ .

A 0.0084% solution of the l perchlorate after oxidation gave  $\alpha_D = -0.07^\circ$  and  $\alpha_{5461} = -0.29^\circ$ ; whence the specific rotation of the l form of the ion  $\text{Ru(phenan)}_3^{+++}$   $[\alpha]_D^{20} = -568^\circ$  and  $[\alpha]_{5461}^{20} = -2354^\circ$ .

## SUMMARY.

The resolution of tris-o-phenanthroline ruthenium perchlorate has been carried out through the antimonyl tartrate. The enantiomorphous forms were notably stable, and showed a very large abnormal rotatory dispersion. They were oxidisable to the blue tris-o-phenanthroline ruthenium III cation, which was also optically active. Within the limits imposed by the instability of the system, the redox potentials of the enantiomorphous forms and the racemate were the same.

## ACKNOWLEDGEMENTS.

The authors are indebted to Miss Fildes for the analyses, and to the Research Fund of the University of Sydney for an assistantship that has enabled one of us (E.C.G.) to take part in this investigation.

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## THE CHEMISTRY OF RUTHENIUM.

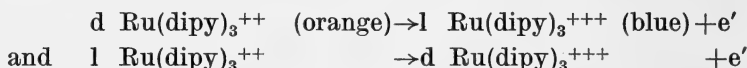
### PART VII. THE OXIDATION OF D AND L TRIS 2 : 2' DIPYRIDYL RUTHENIUM II IODIDE.

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*Manuscript received, September 8, 1949. Read, October 5, 1949.*

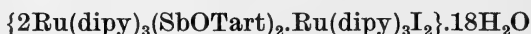
In previous papers (Dwyer and Gyarfás, 1949) it was shown that when d and l tris-o-phenanthroline ruthenium II perchlorates were oxidised with ceric nitrate, the resulting blue solutions of the tris-o-phenanthroline ruthenium III ion were still optically active, but the angles of rotation for the mercury line 5461 and the sodium D line were considerably smaller. It was inferred from these observations that the rotations of the complex ions in the oxidised and reduced forms were not necessarily different but that both ions possessed very large abnormal rotatory dispersions.

The oxidation of the d and l forms of the analogous tris-2 : 2'-dipyridyl ruthenium II ion has now been studied, and it is found that the rotation persists as before but the sign is changed.



After reduction the original ruthenium complex is regenerated, unaltered in the sign or magnitude of the rotation. This unique effect is due to anomalous rotatory dispersion, for the orange ruthenium II complex ion shows no absorption maximum in the visible, whilst that of the blue ruthenium II complex ion is at 5600 Å. The complete absorption and rotatory dispersion curves of this and the analogous iron, osmium and nickel compounds will be described in subsequent communications.

Burstall (1936) resolved tris-2 : 2'-dipyridyl ruthenium II bromide hexahydrate,  $\text{Ru(dipy)}_3\text{Br}_2 \cdot 6\text{H}_2\text{O}$  and found  $[\alpha]_{5791}^{25} = +860^\circ$  and  $-815^\circ$ . The separation was achieved by the use of ammonium d and l tartrates, since the pure laevo form could not be obtained from the mother liquors from which the less soluble d-tris-dipyridyl ruthenium II d tartrate had been crystallised. Since ammonium l tartrate was unavailable it was necessary to devise another procedure for the isolation of the pure laevo form. This was carried out either by fractional crystallisation of the antimonyl tartrate, when the laevo form crystallised first and the dextro form was subsequently isolated as the d tartrate; or more expeditiously as the lattice compound laevo



This curious substance which could be recrystallised either from potassium iodide or potassium antimonyl tartrate solution, crystallised out first when potassium iodide was added to the mixed antimonyl tartrates. It can also be prepared directly by adding potassium antimonyl tartrate to the racemic iodide.

## EXPERIMENTAL.

*The Resolution of Tris-2 : 2-Dipyridyl Ruthenium II Iodide.*

The racemic iodide  $\text{Ru}(\text{dipy})_3\text{I}_2 \cdot 3\text{H}_2\text{O}$  was prepared as described previously (Dwyer, 1949). The iodide (2 g.) in hot water (150 mls.) was transformed to the antimonyl tartrate by shaking with silver antimonyl tartrate (0.9 g.) and filtering from silver iodide and the slight excess of silver antimonyl tartrate. The bright orange-red solution was evaporated to 60 mls. and cooled when 1  $\text{Ru}(\text{dipy})_3(\text{SbO.Tart})_2$  crystallised out. The red crystals were freed from adherent liquid between filter papers, dissolved in N/100 sodium hydroxide (100 mls.) (to destroy the antimonyl tartrate radicle) and precipitated as the iodide by fractional addition of potassium iodide solution. The laevo form was found in the least soluble fractions and purified by recrystallisation from hot water. The mother liquors from the initial antimonyl tartrate solution were precipitated with potassium iodide, and the resulting iodide transformed to the chloride by shaking with silver chloride. The solution of the chloride was then treated with ammonium d tartrate and the dextro form isolated as described by Burstall (*loc. cit.*).

The alternative method, which was found to be more efficient, consisted in taking the antimonyl tartrate solution (100 mls.) prepared from the racemic iodide (2 g.) and fractionally precipitating with dilute potassium iodide solution. The least soluble fractions of red plates and prisms of the lattice compound (*vide supra*) were replaced sharply by much lighter orange-red micaceous plates of the dextro iodide as the fractionation proceeded. An even sharper separation could be achieved by making the solution alkaline with caustic soda as soon as the plates of the dextro form appeared. In this way the antimonyl tartrate radicle was destroyed and only the least soluble dextro iodide precipitated.

The lattice compound was recrystallised either from water, potassium iodide solution or potassium antimonyl tartrate solution—the same substance always being obtained. The crystals became scarlet red in a desiccator or on warming, but regained their lighter colour on standing in moist air. The pure laevo iodide was obtained by solution in sodium hydroxide solution, followed by addition of potassium iodide.

The d and l iodides were crystallised several times from hot water and obtained finally in orange-red micaceous plates.

A 0.0408% solution of the lattice compound in water gave  $\alpha_D^{20} = -0.47^\circ$  (2 dm. tube), whence  $[\alpha]_D^{20} = -576^\circ$ .

A 0.040% solution of the laevo iodide in water in a 2 dm. tube gave  $\alpha_D^{20} = -0.655^\circ$  and  $\alpha_{5461}^{20} = -0.62^\circ$ , whence  $[\alpha]_D^{20} = -819^\circ$  and  $[\alpha]_{5461}^{20} = -775^\circ$ .

A 0.040% solution of the dextro iodide in water gave  $\alpha_D^{20} = +0.656^\circ$  and  $\alpha_{5461}^{20} = +0.62^\circ$ ,  $[\alpha] = +820^\circ$  and  $[\alpha]_{5461}^{20} = +775^\circ$ .

*Analytical Data.*

Found: I = 7.4%; Sb = 14.05%; N = 7.34%.

Calculated for  $2\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_3(\text{SbO.C}_4\text{H}_4\text{O}_6)_2 \cdot \text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_3\text{I}_2 \cdot 18\text{H}_2\text{O}$ : I = 7.35%; Sb = 14.18%; N = 7.34%.

Found, for d form: Ru = 11.60%. Calculated for  $\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_3\text{I}_2 \cdot 3\text{H}_2\text{O}$ : Ru = 11.56%.

*The Oxidation of d and l Tris-Dipyridyl Ruthenium III Iodides.*

Solutions of the d and l iodides (0.02%) in 1 N sulphuric acid were oxidised with solid ceric ammonium nitrate. The orange solutions first became brown due to the liberation of iodine, which was then further oxidised to iodate and then blue coloured due to the  $\text{Ru}(\text{dipy})_3^{+++}$  ion. The oxidised solutions were immediately examined for rotation.

l form (oxidised)  $\alpha_D^{20} = +0.11^\circ$  (2 dm. tube),  $\alpha_{5461}^{20} = +0.08^\circ$  (2 dm. tube)

d form (oxidised)  $\alpha_D^{20} = -0.12^\circ$  (2 dm. tube),  $\alpha_{5461}^{20} = -0.07^\circ$  (2 dm. tube).

The specific rotations of the oxidised solutions for the ion  $\text{Ru}(\text{dipy})_3^{+++}$  compared with the ion  $\text{Ru}(\text{dipy})_3^{++}$  are shown in the table below.

Ion.	$[\alpha]_{\text{D}}^{20}$	$[\alpha]_{5461}^{20}$	$[\alpha]_{5791}^{25} *$
d $\text{Ru}(\text{dipy})_3^{+++}$ (by oxidation of l $\text{Ru}(\text{dipy})^{++}$ )	+426°	+310°	—
l $\text{Ru}(\text{dipy})^{+++}$ (by oxidation of d $\text{Ru}(\text{dipy})_3^{++}$ )	—465°	—271°	—
d $\text{Ru}(\text{dipy})_3^{++}$ .. .. .	+1269°	+1200°	+1264°
l $\text{Ru}(\text{dipy})_3^{++}$ .. .. .	—1270°	—1200°	—1198°

\* Calculated from Burstall (*loc. cit.*).

After the rotations were determined the solutions were reduced by the careful addition of ferrous sulphate crystals, and the original ruthenium II complex was regenerated with its rotation unchanged in each instance. During the time of the measurement, therefore, racemisation had not occurred.

#### SUMMARY.

Tris-dipyridyl ruthenium II iodide has been resolved through the curious lattice compound  $\{2\text{Ru}(\text{dipy})_3(\text{SbO.Tart})_2.\text{Ru}(\text{dipy})_3\text{I}_2\}18\text{H}_2\text{O}$ . The d and l forms when oxidised with ceric nitrate underwent inversion of the sign of the rotation for both the  $\text{NaD}$  and  $\text{Hg}_{5461}$  lines due to the change in the absorption spectrum in passing from the ion  $\text{Ru}(\text{dipy})_3^{++}$  to  $\text{Ru}(\text{dipy})_3^{+++}$ , and the original rotation was regained in sign and magnitude on reduction.

#### ACKNOWLEDGEMENTS.

The authors are indebted to Dr. F. Lions for the preparation of dipyridyl, to Miss J. Fildes for microanalyses, and one of us (E.C.G.) is indebted to the Research Committee of the University of Sydney for a research assistantship.

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# COMPLEX COMPOUNDS OF AUROUS HALIDES AND AUROUS CYANIDE WITH DIPHENYLMETHYL AND DIMETHYLPHENYL ARSINE.

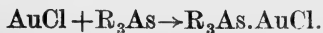
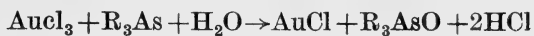
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and D. M. STEWART, B.Sc.

*Manuscript received, September 8, 1949. Read, October 5, 1949.*

The tertiary aliphatic arsine and phosphine complexes of cuprous, argentous and aurous halides have been described by Mann and Purdie (1936), who found that one molecule of arsine or phosphine was coordinated with the metallic halide. The cuprous and argentous complexes were found to be tetrameric whilst the gold complex was monomeric. The structure of tetrakis moniodo triethylarsine copper I investigated by crystal structure analysis (Mann, Purdie and Wells, 1937*a*) showed that in the macro molecule each copper atom was tetrahedral by reason of iodine bridges, whilst each iodine atom was three covalent. The stability of the silver compound  $[\text{Ag}.\text{IAs}(\text{C}_2\text{H}_5)_2]_4$  was much lower than the copper compound, and in solution extensive dissociation to the two covalent monomeric form occurred. Burrows and Parker (1933) found that the silver halide complexes with diphenylmethyl arsine and dimethylphenylarsine were highly insoluble, and of the form  $\text{Ag}(\text{Ph}_2\text{MeAs})_2.\text{X}$ . With boiling alcohol decomposition occurred with loss of arsine, but evidence was not found for the existence of complexes with only one molecule of arsine coordinated. Recent reinvestigation of these compounds (Dwyer and Savage, 1949) under a variety of conditions also failed to isolate compounds containing only one molecule of arsine. Since the insolubility of the compounds precluded molecular weight determinations, it is not possible to know whether the bis-arsine complexes are polymeric and contain four-covalent silver or are monomeric with the silver atom three-covalent. It is significant that Burrows and Sandford (1936), operating with the same two arsines, were able to isolate cuprous halide complexes which contained only one molecule of the arsine and were monomeric, suggesting that the type of arsine coordinated has some influence on the possibility of polymeric molecules.

The aurous halide complexes with tertiary arsines and phosphines were thoroughly studied by Mann and Purdie and Wells (1937*b*) and were found to be monomeric, of the type  $\text{R}_3\text{As}.\text{Aux}$  ( $\text{R}=\text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$ ;  $\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{CNS}$ ) and contained two covalent gold. Many of these compounds were notably stable, and could be distilled under vacuum.

In the present investigation it was thought valuable to determine whether the arsines used by Burrows and Sandford (*loc. cit.*) would yield the usual kind of gold complex, and whether a greater tendency to polymerisation would occur in the iodo than in the chloro compounds. The aurous chloride complexes were made by allowing two molecules of the arsine to react with one molecule of auric chloride in warm aqueous alcoholic solution when reduction and complex formation occurred rapidly.



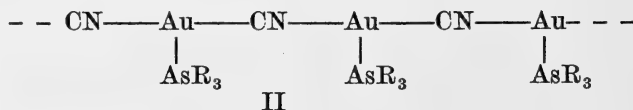
The bromo and iodo compounds were obtained by treatment of the chloro compound with potassium bromide and iodide.

The complexes after crystallisation from aqueous alcohol were obtained as fine white needles, with sharp melting points. Dilute solutions in benzene were monomeric and hence contained two-covalent gold, but the iodide showed a pronounced tendency towards association in concentrated solution. A 2.5% solution had almost doubled the calculated molecular weight and, if it is assumed that tetrameric molecules were formed, was nearly 40% associated into these macro molecules. It is evident that the stronger bonding power of the iodine atom has an important influence on the formation of associated molecules of the type described for the copper and silver complexes.

The coordination compounds of gold I, silver I and Copper I cyanides do not appear to have been investigated hitherto. They should be of special interest because of the linear  $\text{—CN—}$  bonds on the one hand and the high bonding power of the CN group on the other. Whilst silver and cuprous cyanide both dissolve in alcoholic solutions of tertiary arsines, and complex compounds are precipitated on dilution with water or evaporation of the solvent, they lose arsine so easily that they cannot be purified and ultimately decompose completely to the original cyanide (Dwyer and Savage, *loc. cit.*). With aurous cyanide and diphenyl methyl arsine two impure compounds could be obtained:  $\text{AuCN} \cdot 2\text{Ph}_2\text{MeAs}$  I and  $\text{AuCN} \cdot \text{Ph}_2\text{MeAs}$  II. The corresponding compounds with dimethyl phenyl arsine were obtained only as sticky gums and have not been investigated further.

The bis arsine complex I was obtained as a white crystalline substance, easily soluble in organic solvents to colourless solutions, which became yellow on standing or warming and deposited the monoarsine complex II as a pale yellow powder. In freezing bromoform I was dissociated to give a molecular weight almost half of the calculated value. One molecule of arsine was dissociated from the compound and could be easily detected by its odour. The compound I is considered to contain three-covalent gold. It is probable that the silver halide complexes containing two molecules of arsine described by Burrows and Parker (*loc. cit.*) are also three-covalent. It is significant that deposition of the yellow substance II did not occur except on warming, so that apparently a soluble two-covalent complex  $\text{AuCN} \cdot \text{Ph}_2\text{MeAs}$  may exist in solution as an unstable compound. With excess arsine this compound apparently passes into I or alternatively passes into the yellow substance II, which from its insolubility in all solvents, including boiling nitrobenzene, is considered to be polymeric.

The substance II is formulated as containing three-covalent gold through an infinite chain of  $\text{—Au—CN—Au—CN—}$  groups. The ease of transformation of II into I by treatment with excess arsine, and the loss of arsine from II by continued boiling with organic solvents to yield almost pure aurous cyanide are consistent with this formulation.



An investigation is now being made of the aurous, cuprous and silver halide and cyanide complexes with diarsines such as ethylene bis-diphenyl arsine and ethylene bis phenylmethyl arsine, which should provide further evidence of the existence of three covalent complexes of these metals.

#### EXPERIMENTAL.

Auric chloride solution (50 mls.—1% with respect to Au) was mixed with alcohol (20 mls.) and heated to 50° C. The arsine (2 mols.) in alcohol (20 mls.) was added gradually to the warm gold solution with constant stirring. The yellow colour was soon discharged and a colourless



solution of the chloro complex resulted. The bromo or iodo complexes were formed by adding 5 mls. of 10% KBr or KI solution and keeping the solution warm for 10 minutes. Water was finally added until a permanent opalescence resulted—and the mixture allowed to cool slowly. The addition of a little petroleum ether dissolved traces of unreacted arsine and prevented the formation of gums or oils. The white crystalline products were crystallised from warm aqueous alcohol. The series prepared from  $\text{PhMe}_2\text{As}$  crystallised as needles, and from  $\text{Ph}_2\text{MeAs}$  as plates.

$\text{PhMe}_2\text{As}.\text{AuCl}$ , m.p. $121^\circ\text{C}$ .	$\text{Ph}_2\text{MeAs}.\text{AuCl}$ , m.p. $121^\circ\text{C}$ .
$\text{PhMe}_2\text{As}.\text{AuBr}$ , m.p. $120.5^\circ\text{C}$ .	$\text{Ph}_2\text{MeAs}.\text{AuBr}$ , m.p. $118.5^\circ\text{C}$ .
$\text{PhMe}_2\text{As}.\text{AuI}$ , m.p. $130.5^\circ\text{C}$ .	$\text{Ph}_2\text{MeAs}.\text{AuI}$ , m.p. $128^\circ\text{C}$ .

All were soluble in chloroform, benzene, acetone, sparingly soluble in petroleum ether and glacial acetic acid, and insoluble in water. Prolonged heating in any of these solvents led to decomposition and precipitation of gold. Dilute solutions in light became purple or brown, as do the crystals.

TABLE I.  
*Analytical Data.*

Compound.	Au.		Halogen.		C.		H.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
$\text{PhMe}_2\text{As}.\text{AuCl}$ ..	48.5	47.65	8.63	8.56	22.96	23.15	2.80	2.65
$\text{PhMe}_2\text{As}.\text{AuBr}$ ..	42.8	42.9	17.32	17.40	20.31	20.90	2.52	2.41
$\text{PhMe}_2\text{As}.\text{AuI}$ ..	39.15	39.0	24.53	25.15	19.09	18.98	2.30	2.18
$\text{Ph}_2\text{MeAs}.\text{AuCl}$ ..	41.0	41.4	7.53	7.45	32.85	32.75	2.87	2.72
$\text{Ph}_2\text{MeAs}.\text{AuBr}$ ..	37.0	37.8	15.48	15.37	30.50	30.00	2.63	2.49
$\text{Ph}_2\text{MeAs}.\text{AuI}$ ..	34.1	34.75	21.56	22.35	27.08	27.48	2.25	2.29

TABLE II.  
*Molecular Weights.*

	$\text{PhMe}_2\text{As}.\text{AuI}$ .			$\text{Ph}_2\text{MeAs}.\text{AuCl}$ .		
Concentration .. ..	0.025 M	0.04 M	0.051 M	0.02 M	0.07 M	0.08 M
Molecular weight ..	602	652	756	451	504	543
Calculated molecular weight .. ..	—	506	—	—	477	—

#### *I. Bis-diphenyl Methyl Arsine Gold I Cyanide.*

Auric chloride solution (50 mls.—1% with respect to Au) was treated with diphenylmethyl arsine (1.85 g.—3 mols.) in alcohol (30 mls.) followed by potassium cyanide (0.17 g.) dissolved in water (10 mls.). Water was then added in excess and the resulting white oil became solid on shaking with petroleum ether. It was recrystallised from aqueous alcohol containing a little arsine and the white crystals washed with a little petroleum ether. This washing could not be carried to completion without decomposing the compound. The substance melted at  $91^\circ\text{C}$ . It was soluble in benzene, chloroform, alcohol and acetone, but on heating in any of these solvents decomposed with the separation of the yellow form. The solid was unstable and gradually became yellow with the development of the odour of arsine.

Found: Au=29.2%, 26.6%; C=46.1%; H=3.8%. Molecular weight in bromoform from ebullioscopic measurements: 376, 441, 516 for 0.018 M, 0.03 M, 0.04 M solutions, respectively.

Calculated for  $\text{AuCN} \cdot 2(\text{C}_6\text{H}_5)_2\text{CH}_3\text{As}$ : Au = 27.73%; C = 45.5%; H = 3.68%. Molecular weight = 712.

## II. Diphenylmethylarsine Gold I Cyanide.

This substance could be prepared like the compound above by using 2 mols. of arsine and warming the mixture or preferably by boiling I in benzene or alcohol solution. It could not be recrystallised, being insoluble in all solvents even in nitrobenzene. It dissolved in alcohol and arsine to form a colourless solution of I. On heating, the substance became viscous at about 85° C. and decomposed at about 280° C. The compound could not be obtained pure, as it appeared to be always contaminated with aurous cyanide. The latter substance could be isolated almost pure by very long boiling of II with bromobenzene.

Found: Au = 84.46, 84.42%. Calculated for  $\text{AuCN}$ : Au = 84.43%.

Found: Au = 45.2, 46.7%. Calculated for  $(\text{AuCN} \cdot (\text{C}_6\text{H}_5)_2\text{CH}_3\text{As})_n$ : Au = 42.20%.

## SUMMARY.

Aurous halides react with diphenylmethylarsine and dimethylphenylarsine to yield complexes of the type  $\text{AuX} \cdot \text{AsR}_3$ . There is evidence of polymerisation of the iodo compound in concentrated solution—possibly due to the formation of tetrameric molecules. With aurous cyanide two complexes were obtained, a yellow, highly insoluble probably polymeric substance— $(\text{AuCN} \cdot \text{Ph}_2\text{MeAs})^*$ —and an unstable white substance containing two molecules of arsine in which the gold atom is three-covalent.

## ACKNOWLEDGEMENTS.

The authors are indebted to Miss J. Fildes and Miss E. C. Gyrfas for some of the analyses.

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## KEPLER'S PROBLEM—THE PARABOLIC CASE.

By HARLEY WOOD, M.Sc.

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The solution of the parabolic case of Keplerian motion is given by

$$12\mu + \mu^3 = 12\sqrt{2}kq^{-3/2}t = D = 0.29192930q^{-3/2}t$$

where, in the notation of a former paper (Wood, 1950),  $\mu = 2 \tan v/2$  and, with the constant given,  $t$  is in days. The solution of this equation is needed not only for the parabolic orbit but also to give a first approximation in the case of a nearly parabolic ellipse or hyperbola.

In order to disclose the range of variables for which solution is commonly necessary an examination was made of the orbits which do occur. The lists of comet orbits of Galle (1894), Chambers (1889 and 1909), Winlock (1896) and Crommelin (1925 and 1932) and the comet notes of current journals for 1931 to 1940 were examined.

Any tabulation naturally proceeds from perihelion ( $t=0$ ) and carries on as far as the computer may think desirable. Two of the most convenient existing tables, those of Strömgren (1927) and Subbotin (1929), give  $\tan v/2$  with argument  $B(=tq^{-3/2})$  as far as  $B=300$ . From the above list those comets having parabolic or nearly parabolic orbits were selected which had been observed in a part of their orbit for which  $B>300$ . From this list was taken the only one (Halley's) for which the solution in the elliptical form becomes appropriate before  $B$  reaches 300—incidentally no comet with a hyperbolic orbit has been observed beyond the zone of applicability of the nearly parabolic solution. This left 36 comets for which a solution with  $B>300$  was necessary, the extreme value of  $B$  corresponding to an observation being 377,000 for comet 1882 II.

There is a strong tendency for the average period of observation of comets to increase. The following table gives the average duration of visibility of comets (omitting Halley's and Schwassmam—Wachmann 1925 II). During successive twenty-year periods.

Period.	Number of Comets.	Mean Duration of Visibility (in Days).
1851 to 1870 .. ..	76	75
1871 to 1890 .. ..	92	95
1891 to 1910 .. ..	94	115
1911 to 1930 .. ..	103	131

This tendency continues, due to the effort of several observers, notably van Biesbroeck, to extend observed orbital arcs by the use of large telescopes.

CRITICAL TABLE OF  $n(1-n)/2$ .

$n$	$\frac{n(1-n)}{2}$	$n$	$n$	$\frac{n(1-n)}{2}$	$n$	$n$	$\frac{n(1-n)}{2}$	$n$	$n$	$\frac{n(1-n)}{2}$	$n$
0.0000	<b>0.000</b>	1.0000	0.0675	<b>0.032</b>	0.9325	0.1492	<b>0.064</b>	0.8508	0.2571	<b>0.096</b>	0.7429
.0010	<b>.001</b>	0.9990	.0698	<b>.033</b>	.9302	.1521	<b>.065</b>	.8479	.2612	<b>.097</b>	.7388
.0030	<b>.002</b>	.9970	.0722	<b>.034</b>	.9278	.1550	<b>.066</b>	.8450	.2654	<b>.098</b>	.7346
.0050	<b>.003</b>	.9950	.0745	<b>.035</b>	.9255	.1579	<b>.067</b>	.8421	.2697	<b>.099</b>	.7303
.0070	<b>.004</b>	.9930	.0769	<b>.036</b>	.9231	.1608	<b>.068</b>	.8392	.2741	<b>.100</b>	.7259
.0090	<b>.005</b>	.9910	.0792	<b>.037</b>	.9208	.1638	<b>.069</b>	.8362	.2786	<b>.101</b>	.7214
.0111	<b>.006</b>	.9889	.0816	<b>.038</b>	.9184	.1668	<b>.070</b>	.8332	.2832	<b>.102</b>	.7168
.0131	<b>.007</b>	.9869	.0840	<b>.039</b>	.9160	.1698	<b>.071</b>	.8302	.2878	<b>.103</b>	.7122
.0152	<b>.008</b>	.9848	.0864	<b>.040</b>	.9136	.1728	<b>.072</b>	.8272	.2926	<b>.104</b>	.7074
.0172	<b>.009</b>	.9828	.0889	<b>.041</b>	.9111	.1759	<b>.073</b>	.8241	.2975	<b>.105</b>	.7025
.0193	<b>.010</b>	.9807	.0913	<b>.042</b>	.9087	.1790	<b>.074</b>	.8210	.3025	<b>.106</b>	.6975
.0214	<b>.011</b>	.9786	.0937	<b>.043</b>	.9063	.1821	<b>.075</b>	.8179	.3076	<b>.107</b>	.6924
.0235	<b>.012</b>	.9765	.0962	<b>.044</b>	.9038	.1853	<b>.076</b>	.8147	.3129	<b>.108</b>	.6871
.0256	<b>.013</b>	.9744	.0987	<b>.045</b>	.9013	.1885	<b>.077</b>	.8115	.3183	<b>.109</b>	.6817
.0277	<b>.014</b>	.9723	.1012	<b>.046</b>	.8988	.1917	<b>.078</b>	.8083	.3239	<b>.110</b>	.6761
.0298	<b>.015</b>	.9702	.1037	<b>.047</b>	.8963	.1950	<b>.079</b>	.8050	.3297	<b>.111</b>	.6703
.0320	<b>.016</b>	.9680	.1062	<b>.048</b>	.8938	.1983	<b>.080</b>	.8017	.3356	<b>.112</b>	.6644
.0341	<b>.017</b>	.9659	.1088	<b>.049</b>	.8912	.2016	<b>.081</b>	.7984	.3418	<b>.113</b>	.6582
.0363	<b>.018</b>	.9637	.1114	<b>.050</b>	.8886	.2050	<b>.082</b>	.7950	.3483	<b>.114</b>	.6517
.0384	<b>.019</b>	.9616	.1139	<b>.051</b>	.8861	.2084	<b>.083</b>	.7916	.3550	<b>.115</b>	.6450
.0406	<b>.020</b>	.9594	.1165	<b>.052</b>	.8835	.2119	<b>.084</b>	.7881	.3621	<b>.116</b>	.6379
.0428	<b>.021</b>	.9572	.1192	<b>.053</b>	.8808	.2153	<b>.085</b>	.7847	.3696	<b>.117</b>	.6304
.0450	<b>.022</b>	.9550	.1218	<b>.054</b>	.8782	.2189	<b>.086</b>	.7811	.3775	<b>.118</b>	.6225
.0472	<b>.023</b>	.9528	.1245	<b>.055</b>	.8755	.2225	<b>.087</b>	.7775	.3859	<b>.119</b>	.6141
.0494	<b>.024</b>	.9506	.1271	<b>.056</b>	.8729	.2261	<b>.088</b>	.7739	.3951	<b>.120</b>	.6049
.0516	<b>.025</b>	.9484	.1298	<b>.057</b>	.8702	.2298	<b>.089</b>	.7702	.4051	<b>.121</b>	.5949
.0539	<b>.026</b>	.9461	.1325	<b>.058</b>	.8675	.2335	<b>.090</b>	.7665	.4163	<b>.122</b>	.5837
.0561	<b>.027</b>	.9439	.1353	<b>.059</b>	.8647	.2373	<b>.091</b>	.7627	.4292	<b>.123</b>	.5708
.0584	<b>.028</b>	.9416	.1380	<b>.060</b>	.8620	.2411	<b>.092</b>	.7589	.4452	<b>.124</b>	.5548
.0606	<b>.029</b>	.9394	.1408	<b>.061</b>	.8592	.2450	<b>.093</b>	.7550	.4683	<b>.125</b>	.5317
.0629	<b>.030</b>	.9371	.1436	<b>.062</b>	.8564	.2490	<b>.094</b>	.7510	.5316	<b>.124</b>	.4684
.0652	<b>0.031</b>	.9348	.1464	<b>0.063</b>	.8536	.2530	<b>0.095</b>	.7470	.5547	<b>0.123</b>	.4453
0.0675		0.9325	0.1492		0.8508	0.2571		0.7429	0.5707		0.4293

In critical cases take the value of  $n(1-n)/2$  lying higher on the page.

$$\mu_n = (1-n)\mu_0 + n\mu_1 - \frac{n(1-n)}{2}\delta^2\mu_0$$

 $\delta^2\mu_0$  is always negative.



The argument to be used for tables given here is  $D$  ( $3.42 \dots D=B$ ) and the values of  $D$  corresponding to greatest observed distances from perihelion of the comets in the period 1851-1940 are distributed as follows :

Max $D$ .	Number of Comets.
100 to 200 ..	14
200 to 400 ..	6
400 to 1000 ..	3
> 1000 ..	7

If we try to relate the period of visibility of comets to the perihelion distance we find that for perihelion distances from 0 to about 1.4 units the average duration remains nearly constant at about 90 days but with  $q$  between 1.6 and 2.0 units they have an average period of visibility of about 250 days which thereafter falls off.

In the circumstances large values of  $D$  are very probable for comets of small perihelion distance and all of the comets in the above list having max  $D > 100$  have  $q$  small. Although the existing tables cover the majority of cases and it would be impracticable to give full tabulation as far as the extreme case, it is nevertheless desirable to have convenient processes to deal with any case that may occur, especially in view of the increased capacity to observe comets at great distances.

Below are tabulated two methods of solving the parabolic equation. Table 1 was formed by calculating approximate values of  $\mu$  at ten times the interval of the table (except for small portions where five times was necessary) using the tables of Oppolzer (1886). These were corrected by an iterative process to give values accurate to two places beyond what is given in Table 1, differenced and subtabulated to the interval of the table. It is intended that errors will not exceed 0.52 unit of the last recorded place.

The first part of Table 1 gives  $\mu$  to seven decimal places at interval 0.1 of  $D$  up to 100 and the second part ( $100 < D < 1000$ ) at interval 1 gives  $\mu$  to six decimals. The effect of the third difference being negligible throughout the table we may interpolate with the Newton-Gauss formula

$$\mu_n = (1-n)\mu_0 + n\mu_1 - \frac{n(1-n)}{2}\delta^2\mu_0$$

where  $n$  is the fraction of the interval to be interpolated.  $\delta^2\mu$  is given in Table 1 where it is appreciable and when linear interpolation is possible the first difference is tabulated. The coefficient of the second difference is given in the Critical Table on the interleaved flap.

There are two points for comment about this table. It would have been possible to form a table at a closer interval not requiring the use of second differences ; but using a calculating machine with an easily accessible list of second difference coefficients involves very little more work (only a few seconds) than linear interpolation and the time for the determination of  $\mu$  has already, by such a table as this, been reduced to only a small proportion of the time needed to produce one ephemeris place. The extra bulk of table required to avoid the use of second differences seems unjustifiable. Also, an argument much used in tables of parabolic motion is  $tq^{-3/2}$ , but, with  $12\sqrt{2}kq^{-3/2}$  pre-computed for the orbit, the argument adopted here involves no extra time and

TABLE 1.

D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$
0.0	0.000 0000	0	5.0	0.410 8859	125	10.0	0.791 9429	178	15.0	1.129 8170	171
0.1	0.008 3333	3	5.1	0.418 8755	129	10.1	0.799 1378	178	15.1	1.136 1258	171
0.2	0.016 6663	6	5.2	0.426 8522	129	10.2	0.806 3149	177	15.2	1.142 4175	169
0.3	0.024 9987	9	5.3	0.434 8160	132	10.3	0.813 4743	180	15.3	1.148 6923	170
0.4	0.033 3302	11	5.4	0.442 7666	133	10.4	0.820 6157	177	15.4	1.154 9501	169
0.5	0.041 6606	14	5.5	0.450 7039	135	10.5	0.827 7394	180	15.5	1.161 1910	169
0.6	0.049 9896	18	5.6	0.458 6277	136	10.6	0.834 8451	179	15.6	1.167 4150	168
0.7	0.058 3168	20	5.7	0.466 5379	139	10.7	0.841 9329	179	15.7	1.173 6222	168
0.8	0.066 6420	23	5.8	0.474 4342	139	10.8	0.849 0028	179	15.8	1.179 8126	167
0.9	0.074 9649	26	5.9	0.482 3166	142	10.9	0.856 0548	180	15.9	1.185 9863	167
1.0	0.083 2852	29	6.0	0.490 1848	142	11.0	0.863 0888	179	16.0	1.192 1433	166
1.1	0.091 6026	31	6.1	0.498 0388	145	11.1	0.870 1049	180	16.1	1.198 2837	166
1.2	0.099 9169	35	6.2	0.505 8783	146	11.2	0.877 1030	179	16.2	1.204 4075	165
1.3	0.108 2277	37	6.3	0.513 7032	147	11.3	0.884 0832	181	16.3	1.210 5148	165
1.4	0.116 5348	40	6.4	0.521 5134	149	11.4	0.891 0453	179	16.4	1.216 6056	165
1.5	0.124 8379	43	6.5	0.529 3087	149	11.5	0.897 9895	179	16.5	1.222 6799	163
1.6	0.133 1367	46	6.6	0.537 0891	152	11.6	0.904 9158	181	16.6	1.228 7379	163
1.7	0.141 4309	48	6.7	0.544 8543	153	11.7	0.911 8240	179	16.7	1.234 7796	163
1.8	0.149 7203	51	6.8	0.552 6042	153	11.8	0.918 7143	179	16.8	1.240 8050	162
1.9	0.158 0046	54	6.9	0.560 3388	156	11.9	0.925 5867	181	16.9	1.246 8142	162
2.0	0.166 2835	56	7.0	0.568 0578	156	12.0	0.932 4410	178	17.0	1.252 8072	161
2.1	0.174 5568	60	7.1	0.575 7612	157	12.1	0.939 2775	180	17.1	1.258 7841	160
2.2	0.182 8241	62	7.2	0.583 4489	159	12.2	0.946 0960	179	17.2	1.264 7450	161
2.3	0.191 0852	64	7.3	0.591 1207	159	12.3	0.952 8966	180	17.3	1.270 6898	159
2.4	0.199 3399	67	7.4	0.598 7766	162	12.4	0.959 6792	178	17.4	1.276 6187	160
2.5	0.207 5879	70	7.5	0.606 4163	161	12.5	0.966 4440	179	17.5	1.282 5316	157
2.6	0.215 8289	73	7.6	0.614 0399	162	12.6	0.973 1909	179	17.6	1.288 4288	159
2.7	0.224 0626	75	7.7	0.621 6473	165	12.7	0.979 9199	178	17.7	1.294 3101	157
2.8	0.232 2888	77	7.8	0.629 2382	163	12.8	0.986 6311	179	17.8	1.300 1757	156
2.9	0.240 5073	80	7.9	0.636 8128	167	12.9	0.993 3244	177	17.9	1.306 0257	157
3.0	0.248 7178	82	8.0	0.644 3707	166	13.0	1.000 0000	178	18.0	1.311 8600	156
3.1	0.256 9201	85	8.1	0.651 9120	167	13.1	1.006 6578	178	18.1	1.317 6787	155
3.2	0.265 1139	88	8.2	0.659 4366	168	13.2	1.013 2978	177	18.2	1.323 4819	154
3.3	0.273 2989	90	8.3	0.666 9444	168	13.3	1.019 9201	177	18.3	1.329 2697	154
3.4	0.281 4749	91	8.4	0.674 4354	171	13.4	1.026 5247	177	18.4	1.335 0421	154
3.5	0.289 6418	95	8.5	0.681 9093	169	13.5	1.033 1116	176	18.5	1.340 7991	153
3.6	0.297 7992	97	8.6	0.689 3663	172	13.6	1.039 6809	176	18.6	1.346 5408	152
3.7	0.305 9469	99	8.7	0.696 8061	171	13.7	1.046 2326	176	18.7	1.352 2673	152
3.8	0.314 0847	102	8.8	0.704 2288	172	13.8	1.052 7667	176	18.8	1.357 9786	151
3.9	0.322 2123	103	8.9	0.711 6343	173	13.9	1.059 2832	175	18.9	1.363 6748	150
4.0	0.330 3296	106	9.0	0.719 0225	173	14.0	1.065 7822	174	19.0	1.369 3560	151
4.1	0.338 4363	108	9.1	0.726 3934	175	14.1	1.072 2638	175	19.1	1.375 0221	149
4.2	0.346 5322	110	9.2	0.733 7468	173	14.2	1.078 7279	175	19.2	1.380 6733	149
4.3	0.354 6171	112	9.3	0.741 0829	176	14.3	1.085 1745	173	19.3	1.386 3096	149
4.4	0.362 6908	114	9.4	0.748 4014	175	14.4	1.091 6038	173	19.4	1.391 9310	147
4.5	0.370 7531	117	9.5	0.755 7024	176	14.5	1.098 0158	173	19.5	1.397 5377	147
4.6	0.378 8037	118	9.6	0.762 9858	176	14.6	1.104 4105	173	19.6	1.403 1297	147
4.7	0.386 8425	120	9.7	0.770 2516	177	14.7	1.110 7879	172	19.7	1.408 7070	146
4.8	0.394 8693	123	9.8	0.777 4997	176	14.8	1.117 1481	172	19.8	1.414 2697	146
4.9	0.402 8838	124	9.9	0.784 7302	178	14.9	1.123 4911	171	19.9	1.419 8178	144
5.0	0.410 8859	125	10.0	0.791 9429	178	15.0	1.129 8170	171	20.0	1.425 3515	145

TABLE 1.

D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$
20.0	1.425 3515	145	25.0	1.684 8004	116	30.0	1.914 8811	95	35.0	2.121 2503	76
20.1	1.430 8707	144	25.1	1.689 6689	116	30.1	1.919 2241	93	35.1	2.125 1682	77
20.2	1.436 3755	142	25.2	1.694 5258	117	30.2	1.923 5578	95	35.2	2.129 0784	76
20.3	1.441 8661	144	25.3	1.699 3710	116	30.3	1.927 8820	92	35.3	2.132 9810	75
20.4	1.447 3423	141	25.4	1.704 2046	114	30.4	1.932 1970	93	35.4	2.136 8761	77
20.5	1.452 8044	142	25.5	1.709 0268	115	30.5	1.936 5027	93	35.5	2.140 7635	74
20.6	1.458 2523	141	25.6	1.713 8375	114	30.6	1.940 7991	91	35.6	2.144 6435	76
20.7	1.463 6861	141	25.7	1.718 6368	114	30.7	1.945 0864	93	35.7	2.148 5159	74
20.8	1.469 1058	139	25.8	1.723 4247	113	30.8	1.949 3644	90	35.8	2.152 3809	74
20.9	1.474 5116	139	25.9	1.728 2013	112	30.9	1.953 6334	92	35.9	2.156 2385	75
21.0	1.479 9035	139	26.0	1.732 9667	113	31.0	1.957 8932	90	36.0	2.160 0886	73
21.1	1.485 2815	138	26.1	1.737 7208	111	31.1	1.962 1440	90	36.1	2.163 9314	74
21.2	1.490 6457	137	26.2	1.742 4638	111	31.2	1.966 3858	90	36.2	2.167 7668	73
21.3	1.495 9962	138	26.3	1.747 1957	111	31.3	1.970 6186	90	36.3	2.171 5949	72
21.4	1.501 3329	136	26.4	1.751 9165	110	31.4	1.974 8424	88	36.4	2.175 4158	74
21.5	1.506 6560	136	26.5	1.756 6263	110	31.5	1.979 0574	89	36.5	2.179 2293	71
21.6	1.511 9655	135	26.6	1.761 3251	109	31.6	1.983 2635	88	36.6	2.183 0357	73
21.7	1.517 2615	134	26.7	1.766 0130	109	31.7	1.987 4608	88	36.7	2.186 8348	72
21.8	1.522 5441	135	26.8	1.770 6900	109	31.8	1.991 6493	88	36.8	2.190 6267	71
21.9	1.527 8132	133	26.9	1.775 3561	107	31.9	1.995 8290	87	36.9	2.194 4115	71
22.0	1.533 0690	134	27.0	1.780 0115	107	32.0	2.000 0000	87	37.0	2.198 1892	71
22.1	1.538 3114	132	27.1	1.784 6562	108	32.1	2.004 1623	86	37.1	2.201 9598	70
22.2	1.543 5406	132	27.2	1.789 2901	105	32.2	2.008 3160	86	37.2	2.205 7234	71
22.3	1.548 7566	131	27.3	1.793 9135	107	32.3	2.012 4611	86	37.3	2.209 4799	70
22.4	1.553 9595	131	27.4	1.798 5262	106	32.4	2.016 5976	85	37.4	2.213 2294	70
22.5	1.559 1493	130	27.5	1.803 1283	104	32.5	2.020 7256	86	37.5	2.216 9719	70
22.6	1.564 3261	131	27.6	1.807 7200	105	32.6	2.024 8450	84	37.6	2.220 7074	68
22.7	1.569 4898	128	27.7	1.812 3012	105	32.7	2.028 9560	84	37.7	2.224 4361	70
22.8	1.574 6407	129	27.8	1.816 8719	103	32.8	2.033 0586	84	37.8	2.228 1578	68
22.9	1.579 7787	128	27.9	1.821 4323	103	32.9	2.037 1528	84	37.9	2.231 8727	69
23.0	1.584 9039	127	28.0	1.825 9824	104	33.0	2.041 2386	83	38.0	2.235 5807	68
23.1	1.590 0164	128	28.1	1.830 5221	101	33.1	2.045 3161	83	38.1	2.239 2819	68
23.2	1.595 1161	126	28.2	1.835 0517	103	33.2	2.049 3853	83	38.2	2.242 9763	68
23.3	1.600 2032	125	28.3	1.839 5710	101	33.3	2.053 4462	82	38.3	2.246 6639	67
23.4	1.605 2778	127	28.4	1.844 0802	101	33.4	2.057 4989	82	38.4	2.250 3448	67
23.5	1.610 3397	124	28.5	1.848 5793	101	33.5	2.061 5434	82	38.5	2.254 0190	67
23.6	1.615 3892	124	28.6	1.853 0683	100	33.6	2.065 5797	80	38.6	2.257 6865	67
23.7	1.620 4263	125	28.7	1.857 5473	100	33.7	2.069 6080	82	38.7	2.261 3473	66
23.8	1.625 4509	122	28.8	1.862 0163	100	33.8	2.073 6281	80	38.8	2.265 0015	67
23.9	1.630 4633	124	28.9	1.866 4753	98	33.9	2.077 6402	81	38.9	2.268 6490	65
24.0	1.635 4633	121	29.0	1.870 9245	99	34.0	2.081 6442	79	39.0	2.272 2900	65
24.1	1.640 4512	122	29.1	1.875 3638	98	34.1	2.085 6403	80	39.1	2.275 9245	67
24.2	1.645 4269	122	29.2	1.879 7933	98	34.2	2.089 6284	80	39.2	2.279 5523	64
24.3	1.650 3904	120	29.3	1.884 2130	97	34.3	2.093 6085	78	39.3	2.283 1737	65
24.4	1.655 3419	120	29.4	1.888 6230	97	34.4	2.097 5808	79	39.4	2.286 7886	65
24.5	1.660 2814	119	29.5	1.893 0233	96	34.5	2.101 5452	79	39.5	2.290 3970	64
24.6	1.665 2090	120	29.6	1.897 4140	96	34.6	2.105 5017	77	39.6	2.293 9990	65
24.7	1.670 1246	119	29.7	1.901 7951	96	34.7	2.109 4505	78	39.7	2.297 5945	63
24.8	1.675 0283	117	29.8	1.906 1666	95	34.8	2.113 3915	77	39.8	2.301 1837	64
24.9	1.679 9203	119	29.9	1.910 5286	95	34.9	2.117 3248	78	39.9	2.304 7665	63
25.0	1.684 8004	116	30.0	1.914 8811	95	35.0	2.121 2503	76	40.0	2.308 3430	64



TABLE 1.

D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$
40.0	2.308 3430	64	45.0	2.479 5733	53	50.0	2.637 5754	45	55.0	2.784 4020	38
40.1	2.311 9131	62	45.1	2.482 8553	53	50.1	2.640 6154	44	55.1	2.787 2363	38
40.2	2.315 4770	63	45.2	2.486 1320	52	50.2	2.643 6510	44	55.2	2.790 0668	38
40.3	2.319 0346	63	45.3	2.489 4035	52	50.3	2.646 6822	45	55.3	2.792 8935	38
40.4	2.322 5859	62	45.4	2.492 6698	52	50.4	2.649 7089	43	55.4	2.795 7164	38
40.5	2.326 1310	62	45.5	2.495 9309	52	50.5	2.652 7313	45	55.5	2.798 5355	37
40.6	2.329 6699	62	45.6	2.499 1868	51	50.6	2.655 7492	43	55.6	2.801 3509	37
40.7	2.333 2026	61	45.7	2.502 4376	52	50.7	2.658 7628	44	55.7	2.804 1626	38
40.8	2.336 7292	62	45.8	2.505 6832	52	50.8	2.661 7720	43	55.8	2.806 9705	37
40.9	2.340 2496	61	45.9	2.508 9236	50	50.9	2.664 7769	43	55.9	2.809 7747	37
41.0	2.343 7639	60	46.0	2.512 1590	51	51.0	2.667 7775	44	56.0	2.812 5752	38
41.1	2.347 2722	62	46.1	2.515 3893	51	51.1	2.670 7737	42	56.1	2.815 3719	36
41.2	2.350 7743	59	46.2	2.518 6145	51	51.2	2.673 7657	44	56.2	2.818 1650	36
41.3	2.354 2705	61	46.3	2.521 8346	50	51.3	2.676 7533	42	56.3	2.820 9545	38
41.4	2.357 7606	60	46.4	2.525 0497	50	51.4	2.679 7367	43	56.4	2.823 7402	36
41.5	2.361 2447	60	46.5	2.528 2598	51	51.5	2.682 7158	42	56.5	2.826 5223	36
41.6	2.364 7228	59	46.6	2.531 4648	49	51.6	2.685 6907	42	56.6	2.829 3008	37
41.7	2.368 1950	60	46.7	2.534 6649	50	51.7	2.688 6614	43	56.7	2.832 0756	36
41.8	2.371 6612	58	46.8	2.537 8600	49	51.8	2.691 6278	42	56.8	2.834 8468	36
41.9	2.375 1216	60	46.9	2.541 0502	50	51.9	2.694 5900	42	56.9	2.837 6144	37
42.0	2.378 5760	58	47.0	2.544 2354	49	52.0	2.697 5480	41	57.0	2.840 3783	35
42.1	2.382 0246	59	47.1	2.547 4157	50	52.1	2.700 5019	43	57.1	2.843 1387	36
42.2	2.385 4673	58	47.2	2.550 5910	48	52.2	2.703 4515	40	57.2	2.845 8955	35
42.3	2.388 9042	58	47.3	2.553 7615	48	52.3	2.706 3971	43	57.3	2.848 6488	36
42.4	2.392 3353	58	47.4	2.556 9272	50	52.4	2.709 3384	40	57.4	2.851 3985	36
42.5	2.395 7606	57	47.5	2.560 0879	47	52.5	2.712 2757	42	57.5	2.854 1446	35
42.6	2.399 1802	58	47.6	2.563 2439	49	52.6	2.715 2088	40	57.6	2.856 8872	36
42.7	2.402 5940	57	47.7	2.566 3950	48	52.7	2.718 1379	42	57.7	2.859 6262	34
42.8	2.406 0021	57	47.8	2.569 5413	48	52.8	2.721 0628	40	57.8	2.862 3618	36
42.9	2.409 4045	57	47.9	2.572 6828	48	52.9	2.723 9837	41	57.9	2.865 0938	35
43.0	2.412 8012	57	48.0	2.575 8195	47	53.0	2.726 9005	41	58.0	2.867 8223	34
43.1	2.416 1922	56	48.1	2.578 9515	48	53.1	2.729 8132	40	58.1	2.870 5474	36
43.2	2.419 5776	56	48.2	2.582 0787	47	53.2	2.732 7219	40	58.2	2.873 2689	34
43.3	2.422 9574	56	48.3	2.585 2012	47	53.3	2.735 6266	40	58.3	2.875 9870	34
43.4	2.426 3316	56	48.4	2.588 3190	47	53.4	2.738 5273	40	58.4	2.878 7017	35
43.5	2.429 7002	55	48.5	2.591 4321	47	53.5	2.741 4240	41	58.5	2.881 4129	35
43.6	2.433 0633	56	48.6	2.594 5405	46	53.6	2.744 3166	38	58.6	2.884 1206	34
43.7	2.436 4208	55	48.7	2.597 6443	47	53.7	2.747 2054	41	58.7	2.886 8249	34
43.8	2.439 7728	55	48.8	2.600 7434	47	53.8	2.750 0901	39	58.8	2.889 5258	34
43.9	2.443 1193	55	48.9	2.603 8378	45	53.9	2.752 9709	40	58.9	2.892 2233	34
44.0	2.446 4603	54	49.0	2.606 9277	47	54.0	2.755 8477	39	59.0	2.894 9174	34
44.1	2.449 7959	55	49.1	2.610 0129	45	54.1	2.758 7206	39	59.1	2.897 6081	34
44.2	2.453 1260	54	49.2	2.613 0936	46	54.2	2.761 5896	39	59.2	2.900 2954	33
44.3	2.456 4507	54	49.3	2.616 1697	46	54.3	2.764 4547	39	59.3	2.902 9794	34
44.4	2.459 7700	54	49.4	2.619 2412	45	54.4	2.767 3159	39	59.4	2.905 6600	34
44.5	2.463 0839	54	49.5	2.622 3082	46	54.5	2.770 1732	38	59.5	2.908 3372	33
44.6	2.466 3924	53	49.6	2.625 3706	45	54.6	2.773 0267	39	59.6	2.911 0111	33
44.7	2.469 6956	53	49.7	2.628 4285	44	54.7	2.775 8763	39	59.7	2.913 6817	34
44.8	2.472 9935	54	49.8	2.631 4820	46	54.8	2.778 7220	38	59.8	2.916 3489	33
44.9	2.476 2860	52	49.9	2.634 5309	44	54.9	2.781 5639	38	59.9	2.919 0128	32
45.0	2.479 5733	53	50.0	2.637 5754	45	55.0	2.784 4020	38	60.0	2.921 6735	34

TABLE 1.

D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$
60.0	2.921 6735	34	65.0	3.050 6859	30	70.0	3.172 4896	26	75.0	3.287 9463	21
60.1	2.924 3308	33	65.1	3.053 1894	28	70.1	3.174 8583	25	75.1	3.290 1959	24
60.2	2.926 9848	32	65.2	3.055 6901	28	70.2	3.177 2245	25	75.2	3.292 4431	21
60.3	2.929 6356	33	65.3	3.058 1880	30	70.3	3.179 5882	25	75.3	3.294 6882	23
60.4	2.932 2831	33	65.4	3.060 6829	27	70.4	3.181 9494	25	75.4	3.296 9310	22
60.5	2.934 9273	32	65.5	3.063 1751	29	70.5	3.184 3081	26	75.5	3.299 1716	23
60.6	2.937 5683	33	65.6	3.065 6644	29	70.6	3.186 6642	24	75.6	3.301 4099	22
60.7	2.940 2060	31	65.7	3.068 1508	27	70.7	3.189 0179	26	75.7	3.303 6460	21
60.8	2.942 8406	33	65.8	3.070 6345	29	70.8	3.191 3690	24	75.8	3.305 8800	23
60.9	2.945 4719	33	65.9	3.073 1153	28	70.9	3.193 7177	25	75.9	3.308 1117	22
61.0	2.948 0999	31	66.0	3.075 5933	28	71.0	3.196 0639	24	76.0	3.310 3412	22
61.1	2.950 7248	32	66.1	3.078 0685	28	71.1	3.198 4077	26	76.1	3.312 5685	22
61.2	2.953 3465	32	66.2	3.080 5409	28	71.2	3.200 7489	24	76.2	3.314 7936	22
61.3	2.955 9650	32	66.3	3.083 0105	27	71.3	3.203 0877	24	76.3	3.317 0165	21
61.4	2.958 5803	32	66.4	3.085 4774	28	71.4	3.205 4241	25	76.4	3.319 2373	23
61.5	2.961 1924	31	66.5	3.087 9415	28	71.5	3.207 7580	24	76.5	3.321 4558	21
61.6	2.963 8014	32	66.6	3.090 4028	28	71.6	3.210 0895	25	76.6	3.323 6722	21
61.7	2.966 4072	31	66.7	3.092 8613	27	71.7	3.212 4185	24	76.7	3.325 8865	23
61.8	2.969 0099	31	66.8	3.095 3171	28	71.8	3.214 7451	25	76.8	3.328 0985	21
61.9	2.971 6095	32	66.9	3.097 7701	27	71.9	3.217 0692	23	76.9	3.330 3084	21
62.0	2.974 2059	31	67.0	3.100 2204	27	72.0	3.219 3910	25	77.0	3.332 5162	22
62.1	2.976 7992	31	67.1	3.102 6680	28	72.1	3.221 7103	24	77.1	3.334 7218	21
62.2	2.979 3894	31	67.2	3.105 1128	26	72.2	3.224 0272	23	77.2	3.336 9253	22
62.3	2.981 9765	31	67.3	3.107 5550	28	72.3	3.226 3418	25	77.3	3.339 1266	21
62.4	2.984 5605	31	67.4	3.109 9944	27	72.4	3.228 6539	24	77.4	3.341 3258	22
62.5	2.987 1414	31	67.5	3.112 4311	27	72.5	3.230 9636	23	77.5	3.343 5228	20
62.6	2.989 7192	30	67.6	3.114 8651	27	72.6	3.233 2710	24	77.6	3.345 7178	22
62.7	2.992 2940	31	67.7	3.117 2964	26	72.7	3.235 5760	24	77.7	3.347 9106	21
62.8	2.994 8657	30	67.8	3.119 7251	28	72.8	3.237 8786	24	77.8	3.350 1013	21
62.9	2.997 4344	31	67.9	3.122 1510	26	72.9	3.240 1788	24	77.9	3.352 2899	22
63.0	3.000 0000	30	68.0	3.124 5743	27	73.0	3.242 4766	22	78.0	3.354 4763	20
63.1	3.002 5626	31	68.1	3.126 9949	26	73.1	3.244 7722	25	78.1	3.356 6607	21
63.2	3.005 1221	29	68.2	3.129 4129	27	73.2	3.247 0653	23	78.2	3.358 8430	21
63.3	3.007 6787	31	68.3	3.131 8282	26	73.3	3.249 3561	23	78.3	3.361 0232	21
63.4	3.010 2322	29	68.4	3.134 2409	27	73.4	3.251 6446	24	78.4	3.363 2013	21
63.5	3.012 7828	31	68.5	3.136 6509	25	73.5	3.253 9307	22	78.5	3.365 3773	20
63.6	3.015 3303	30	68.6	3.139 0584	28	73.6	3.256 2146	25	78.6	3.367 5513	21
63.7	3.017 8748	29	68.7	3.141 4631	25	73.7	3.258 4960	22	78.7	3.369 7232	21
63.8	3.020 4164	30	68.8	3.143 8653	26	73.8	3.260 7752	23	78.8	3.371 8930	21
63.9	3.022 9550	29	68.9	3.146 2649	27	73.9	3.263 0521	24	78.9	3.374 0607	20
64.0	3.025 4907	31	69.0	3.148 6618	25	74.0	3.265 3266	23	79.0	3.376 2264	21
64.1	3.028 0233	28	69.1	3.151 0562	26	74.1	3.267 5988	22	79.1	3.378 3900	20
64.2	3.030 5531	30	69.2	3.153 4480	27	74.2	3.269 8688	23	79.2	3.380 5516	21
64.3	3.033 0799	30	69.3	3.155 8371	25	74.3	3.272 1365	24	79.3	3.382 7111	20
64.4	3.035 6037	28	69.4	3.158 2237	25	74.4	3.274 4018	22	79.4	3.384 8686	20
64.5	3.038 1247	30	69.5	3.160 6078	27	74.5	3.276 6649	23	79.5	3.387 0241	21
64.6	3.040 6427	28	69.6	3.162 9892	24	74.6	3.278 9257	22	79.6	3.389 1775	20
64.7	3.043 1579	30	69.7	3.165 3682	27	74.7	3.281 1843	23	79.7	3.391 3289	20
64.8	3.045 6701	29	69.8	3.167 7445	25	74.8	3.283 4406	23	79.8	3.393 4783	21
64.9	3.048 1794	28	69.9	3.170 1183	25	74.9	3.285 6946	23	79.9	3.395 6256	19
65.0	3.050 6859	30	70.0	3.172 4896	26	75.0	3.287 9463	21	80.0	3.397 7710	21

TABLE 1.

D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$
80.0	3.397 7710	21	85.0	3.502 5627	18	90.0	3.602 8285	17	95.0	3.699 0011	14
80.1	3.399 9143	20	85.1	3.504 6108	18	90.1	3.604 7907	16	95.1	3.700 8855	16
80.2	3.402 0556	19	85.2	3.506 6571	18	90.2	3.606 7513	16	95.2	3.702 7683	14
80.3	3.404 1950	21	85.3	3.508 7016	18	90.3	3.608 7103	17	95.3	3.704 6497	15
80.4	3.406 3323	20	85.4	3.510 7443	17	90.4	3.610 6676	15	95.4	3.706 5296	15
80.5	3.408 4676	19	85.5	3.512 7853	19	90.5	3.612 6234	17	95.5	3.708 4080	14
80.6	3.410 6010	21	85.6	3.514 8244	18	90.6	3.614 5775	16	95.6	3.710 2850	15
80.7	3.412 7323	19	85.7	3.516 8617	17	90.7	3.616 5300	17	95.7	3.712 1605	15
80.8	3.414 8617	20	85.8	3.518 8973	18	90.8	3.618 4808	15	95.8	3.714 0345	14
80.9	3.416 9891	20	85.9	3.520 9311	18	90.9	3.620 4301	16	95.9	3.715 9071	16
81.0	3.419 1145	19	86.0	3.522 9631	18	91.0	3.622 3778	17	96.0	3.717 7781	13
81.1	3.421 2380	20	86.1	3.524 9933	17	91.1	3.624 3238	15	96.1	3.719 6478	15
81.2	3.423 3595	20	86.2	3.527 0218	18	91.2	3.626 2683	17	96.2	3.721 5160	15
81.3	3.425 4790	19	86.3	3.529 0485	17	91.3	3.628 2111	15	96.3	3.723 3827	15
81.4	3.427 5966	19	86.4	3.531 0735	18	91.4	3.630 1524	16	96.4	3.725 2479	13
81.5	3.429 7123	20	86.5	3.533 0967	18	91.5	3.632 0921	17	96.5	3.727 1118	16
81.6	3.431 8260	20	86.6	3.535 1181	17	91.6	3.634 0301	15	96.6	3.728 9741	13
81.7	3.433 9377	19	86.7	3.537 1378	18	91.7	3.635 9666	15	96.7	3.730 8351	15
81.8	3.436 0475	19	86.8	3.539 1557	17	91.8	3.637 9016	17	96.8	3.732 6946	15
81.9	3.438 1554	19	86.9	3.541 1719	17	91.9	3.639 8349	16	96.9	3.734 5526	14
82.0	3.440 2614	20	87.0	3.543 1864	18	92.0	3.641 7666	15	97.0	3.736 4092	14
82.1	3.442 3654	19	87.1	3.545 1991	17	92.1	3.643 6968	16	97.1	3.738 2644	14
82.2	3.444 4675	19	87.2	3.547 2101	17	92.2	3.645 6254	15	97.2	3.740 1182	15
82.3	3.446 5677	19	87.3	3.549 2194	18	92.3	3.647 5525	16	97.3	3.741 9705	14
82.4	3.448 6660	20	87.4	3.551 2269	17	92.4	3.649 4780	16	97.4	3.743 8214	14
82.5	3.450 7623	18	87.5	3.553 2327	17	92.5	3.651 4019	15	97.5	3.745 6709	15
82.6	3.452 8568	19	87.6	3.555 2368	17	92.6	3.653 3243	16	97.6	3.747 5189	14
82.7	3.454 9494	20	87.7	3.557 2392	17	92.7	3.655 2451	16	97.7	3.749 3655	13
82.8	3.457 0400	18	87.8	3.559 2399	18	92.8	3.657 1643	15	97.8	3.751 2108	15
82.9	3.459 1288	19	87.9	3.561 2388	16	92.9	3.659 0820	15	97.9	3.753 0546	14
83.0	3.461 2157	19	88.0	3.563 2361	17	93.0	3.660 9982	16	98.0	3.754 8970	14
83.1	3.463 3007	19	88.1	3.565 2317	18	93.1	3.662 9128	15	98.1	3.756 7380	14
83.2	3.465 3838	19	88.2	3.567 2255	16	93.2	3.664 8259	16	98.2	3.758 5776	15
83.3	3.467 4650	18	88.3	3.569 2177	17	93.3	3.666 7374	15	98.3	3.760 4157	13
83.4	3.469 5444	19	88.4	3.571 2082	18	93.4	3.668 6474	15	98.4	3.762 2525	14
83.5	3.471 6219	19	88.5	3.573 1969	16	93.5	3.670 5559	15	98.5	3.764 0879	14
83.6	3.473 6975	18	88.6	3.575 1840	16	93.6	3.672 4629	16	98.6	3.765 9219	14
83.7	3.475 7713	19	88.7	3.577 1695	18	93.7	3.674 3683	15	98.7	3.767 7545	14
83.8	3.477 8432	18	88.8	3.579 1532	16	93.8	3.676 2722	16	98.8	3.769 5857	13
83.9	3.479 9133	19	88.9	3.581 1353	17	93.9	3.678 1745	14	98.9	3.771 4156	15
84.0	3.481 9815	19	89.0	3.583 1157	17	94.0	3.680 0754	16	99.0	3.773 2440	13
84.1	3.484 0478	17	89.1	3.585 0944	16	94.1	3.681 9747	14	99.1	3.775 0711	15
84.2	3.486 1124	20	89.2	3.587 0715	17	94.2	3.683 8726	16	99.2	3.776 8967	13
84.3	3.488 1750	17	89.3	3.589 0469	17	94.3	3.685 7689	15	99.3	3.778 7210	13
84.4	3.490 2359	19	89.4	3.591 0206	16	94.4	3.687 6637	15	99.4	3.780 5440	15
84.5	3.492 2949	18	89.5	3.592 9927	16	94.5	3.689 5570	15	99.5	3.782 3655	13
84.6	3.494 3521	18	89.6	3.594 9632	17	94.6	3.691 4488	15	99.6	3.784 1857	14
84.7	3.496 4075	19	89.7	3.596 9320	17	94.7	3.693 3391	14	99.7	3.786 0045	13
84.8	3.498 4610	17	89.8	3.598 8991	16	94.8	3.695 2280	16	99.8	3.787 8220	14
84.9	3.500 5128	19	89.9	3.600 8646	16	94.9	3.697 1153	15	99.9	3.789 6381	14
85.0	3.502 5627	18	90.0	3.602 8285	17	95.0	3.699 0011	14	100.0	3.791 4528	14

TABLE 1.

D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$
100	3.791 453	136	150	4.566 193	66	200	5.167 521	39	250	5.667 009	28
101	3.809 526	134	151	4.579 574	65	201	5.178 358	39	251	5.676 225	26
102	3.827 465	130	152	4.592 890	66	202	5.189 156	40	252	5.685 415	27
103	3.845 274	130	153	4.606 140	63	203	5.199 914	38	253	5.694 578	25
104	3.862 953	126	154	4.619 327	63	204	5.210 634	38	254	5.703 716	27
105	3.880 506	125	155	4.632 451	62	205	5.221 316	39	255	5.712 827	25
106	3.897 934	122	156	4.645 513	62	206	5.231 959	37	256	5.721 913	26
107	3.915 240	121	157	4.658 513	61	207	5.242 565	37	257	5.730 973	26
108	3.932 425	118	158	4.671 452	61	208	5.253 134	38	258	5.740 007	25
109	3.949 492	117	159	4.684 330	59	209	5.263 665	36	259	5.749 016	25
110	3.966 442	115	160	4.697 149	59	210	5.274 160	36	260	5.758 000	25
111	3.983 277	112	161	4.709 909	58	211	5.284 619	37	261	5.766 959	24
112	4.000 000	112	162	4.722 611	58	212	5.295 041	35	262	5.775 894	26
113	4.016 611	109	163	4.735 255	57	213	5.305 428	36	263	5.784 803	23
114	4.033 113	107	164	4.747 842	56	214	5.315 779	35	264	5.793 689	26
115	4.049 508	107	165	4.760 373	56	215	5.326 095	35	265	5.802 549	23
116	4.065 796	104	166	4.772 848	56	216	5.336 376	35	266	5.811 386	24
117	4.081 980	103	167	4.785 267	54	217	5.346 622	34	267	5.820 199	24
118	4.098 061	101	168	4.797 632	54	218	5.356 834	33	268	5.828 988	23
119	4.114 041	100	169	4.809 943	54	219	5.367 013	35	269	5.837 754	24
120	4.129 921	98	170	4.822 200	52	220	5.377 157	33	270	5.846 496	24
121	4.145 703	98	171	4.834 405	53	221	5.387 268	34	271	5.855 214	22
122	4.161 387	94	172	4.846 557	52	222	5.397 345	32	272	5.863 910	24
123	4.176 977	95	173	4.858 657	51	223	5.407 390	34	273	5.872 582	23
124	4.192 472	92	174	4.870 706	51	224	5.417 401	31	274	5.881 231	22
125	4.207 875	92	175	4.882 704	50	225	5.427 381	33	275	5.889 858	23
126	4.223 186	90	176	4.894 652	50	226	5.437 328	32	276	5.898 462	22
127	4.238 407	89	177	4.906 550	50	227	5.447 243	31	277	5.907 044	23
128	4.253 539	88	178	4.918 398	48	228	5.457 127	32	278	5.915 603	22
129	4.268 583	86	179	4.930 198	48	229	5.466 979	32	279	5.924 140	21
130	4.283 541	85	180	4.941 950	48	230	5.476 799	30	280	5.932 656	23
131	4.298 414	85	181	4.953 654	48	231	5.486 589	31	281	5.941 149	22
132	4.313 202	82	182	4.965 310	46	232	5.496 348	30	282	5.949 620	21
133	4.327 908	83	183	4.976 920	47	233	5.506 077	31	283	5.958 070	21
134	4.342 531	80	184	4.988 483	46	234	5.515 775	30	284	5.966 499	22
135	4.357 074	80	185	5.000 000	45	235	5.525 443	29	285	5.974 906	21
136	4.371 537	78	186	5.011 472	46	236	5.535 082	30	286	5.983 292	22
137	4.385 922	79	187	5.022 898	44	237	5.544 691	30	287	5.991 656	20
138	4.400 228	76	188	5.034 280	45	238	5.554 270	29	288	6.000 000	21
139	4.414 458	75	189	5.045 617	43	239	5.563 820	28	289	6.008 323	21
140	4.428 613	76	190	5.056 911	44	240	5.573 342	30	290	6.016 625	20
141	4.442 692	73	191	5.068 161	43	241	5.582 834	28	291	6.024 907	21
142	4.456 698	73	192	5.079 368	43	242	5.592 298	28	292	6.033 168	20
143	4.470 631	72	193	5.090 532	41	243	5.601 734	28	293	6.041 409	20
144	4.484 492	72	194	5.101 655	43	244	5.611 142	29	294	6.049 630	21
145	4.498 281	69	195	5.112 735	41	245	5.620 521	26	295	6.057 830	19
146	4.512 001	70	196	5.123 774	42	246	5.629 874	29	296	6.066 011	21
147	4.525 651	69	197	5.134 771	40	247	5.639 198	27	297	6.074 171	19
148	4.539 232	67	198	5.145 728	40	248	5.648 495	27	298	6.082 312	19
149	4.552 746	67	199	5.156 645	41	249	5.657 765	26	299	6.090 434	20
150	4.566 193	66	200	5.167 521	39	250	5.667 009	28	300	6.098 536	20

TABLE 1.

D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$
300	6.098 536	20	350	6.481 031	16	400	6.826 234	12	450	7.141 974	10
301	6.106 618	19	351	6.488 269	14	401	6.832 816	12	451	7.148 029	10
302	6.114 681	19	352	6.495 493	15	402	6.839 386	11	452	7.154 074	9
303	6.122 725	19	353	6.502 702	15	403	6.845 945	12	453	7.160 110	9
304	6.130 750	19	354	6.509 896	14	404	6.852 492	11	454	7.166 137	10
305	6.138 756	18	355	6.517 076	14	405	6.859 028	12	455	7.172 154	9
306	6.146 744	20	356	6.524 242	15	406	6.865 552	11	456	7.178 162	9
307	6.154 712	18	357	6.531 393	14	407	6.872 065	11	457	7.184 161	10
308	6.162 662	19	358	6.538 530	15	408	6.878 567	12	458	7.190 150	9
309	6.170 593	18	359	6.545 652	13	409	6.885 057	11	459	7.196 130	9
310	6.178 506	18	360	6.552 761	15	410	6.891 536	11	460	7.202 101	10
311	6.186 401	19	361	6.559 855	13	411	6.898 004	12	461	7.208 062	8
312	6.194 277	17	362	6.566 936	15	412	6.904 460	10	462	7.214 015	10
313	6.202 136	19	363	6.574 002	13	413	6.910 906	12	463	7.219 958	9
314	6.209 976	18	364	6.581 055	14	414	6.917 340	11	464	7.225 892	8
315	6.217 798	17	365	6.588 094	14	415	6.923 763	10	465	7.231 818	10
316	6.225 603	18	366	6.595 119	14	416	6.930 176	12	466	7.237 734	9
317	6.233 390	18	367	6.602 130	13	417	6.936 577	10	467	7.243 641	8
318	6.241 159	17	368	6.609 128	14	418	6.942 968	12	468	7.249 540	10
319	6.248 911	17	369	6.616 112	13	419	6.949 347	10	469	7.255 429	8
320	6.256 646	18	370	6.623 083	14	420	6.955 716	10	470	7.261 310	10
321	6.264 363	17	371	6.630 040	13	421	6.962 075	12	471	7.267 181	8
322	6.272 063	17	372	6.636 984	13	422	6.968 422	10	472	7.273 044	9
323	6.279 746	18	373	6.643 915	14	423	6.974 759	11	473	7.278 898	8
324	6.287 411	16	374	6.650 832	13	424	6.981 085	11	474	7.284 744	10
325	6.295 060	17	375	6.657 736	13	425	6.987 400	10	475	7.290 580	8
326	6.302 692	17	376	6.664 627	13	426	6.993 705	10	476	7.296 408	8
327	6.310 307	16	377	6.671 505	12	427	7.000 000	11	477	7.302 228	9
328	6.317 906	17	378	6.678 371	14	428	7.006 284	10	478	7.308 039	9
329	6.325 488	17	379	6.685 223	13	429	7.012 558	11	479	7.313 841	9
330	6.333 053	15	380	6.692 062	13	430	7.018 821	10	480	7.319 634	8
331	6.340 603	18	381	6.698 888	12	431	7.025 074	10	481	7.325 419	8
332	6.348 135	15	382	6.705 702	13	432	7.031 317	11	482	7.331 196	9
333	6.355 652	17	383	6.712 503	12	433	7.037 549	9	483	7.336 964	8
334	6.363 152	15	384	6.719 292	13	434	7.043 772	11	484	7.342 724	9
335	6.370 637	17	385	6.726 068	13	435	7.049 984	10	485	7.348 475	8
336	6.378 105	15	386	6.732 831	12	436	7.056 186	10	486	7.354 218	8
337	6.385 558	17	387	6.739 582	13	437	7.062 378	10	487	7.359 953	9
338	6.392 994	15	388	6.746 320	12	438	7.068 560	11	488	7.365 679	8
339	6.400 415	16	389	6.753 046	12	439	7.074 731	9	489	7.371 397	8
340	6.407 820	15	390	6.759 760	12	440	7.080 893	10	490	7.377 107	9
341	6.415 210	16	391	6.766 462	13	441	7.087 045	9	491	7.382 808	7
342	6.422 584	15	392	6.773 151	12	442	7.093 188	11	492	7.388 502	9
343	6.429 943	15	393	6.779 828	12	443	7.099 320	10	493	7.394 187	8
344	6.437 287	16	394	6.786 493	11	444	7.105 442	9	494	7.399 864	8
345	6.444 615	15	395	6.793 147	13	445	7.111 555	10	495	7.405 533	8
346	6.451 928	15	396	6.799 788	12	446	7.117 658	9	496	7.411 194	9
347	6.459 226	15	397	6.806 417	12	447	7.123 752	11	497	7.416 846	7
348	6.466 509	15	398	6.813 034	11	448	7.129 835	9	498	7.422 491	8
349	6.473 777	14	399	6.819 640	12	449	7.135 909	9	499	7.428 128	8
350	6.481 031	16	400	6.826 234	12	450	7.141 974	10	500	7.433 757	8

TABLE 1.

D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$	D	$\mu$	$\delta^2$
500	7.433 757	8	550	7.705 616	7	600	7.960 602	6	650	8.201 085	4
501	7.439 378	8	551	7.710 872	6	601	7.965 547	6	651	8.205 761	6
502	7.444 991	8	552	7.716 122	8	602	7.970 486	6	652	8.210 431	5
503	7.450 596	8	553	7.721 364	6	603	7.975 419	5	653	8.215 096	4
504	7.456 193	7	554	7.726 600	6	604	7.980 347	6	654	8.219 757	6
505	7.461 783	9	555	7.731 830	7	605	7.985 269	6	655	8.224 412	5
506	7.467 364	7	556	7.737 053	7	606	7.990 185	6	656	8.229 062	4
507	7.472 938	8	557	7.742 269	6	607	7.995 095	5	657	8.233 708	6
508	7.478 504	8	558	7.747 479	7	608	8.000 000	6	658	8.238 348	4
509	7.484 062	7	559	7.752 682	6	609	8.004 899	5	659	8.242 984	6
510	7.489 613	8	560	7.757 879	7	610	8.009 793	6	660	8.247 614	4
511	7.495 156	7	561	7.763 069	7	611	8.014 681	6	661	8.252 240	5
512	7.500 692	9	562	7.768 252	6	612	8.019 563	6	662	8.256 861	5
513	7.506 219	7	563	7.773 429	6	613	8.024 439	4	663	8.261 477	5
514	7.511 739	7	564	7.778 600	7	614	8.029 311	7	664	8.266 088	5
515	7.517 252	8	565	7.783 764	6	615	8.034 176	5	665	8.270 694	5
516	7.522 757	7	566	7.788 922	6	616	8.039 036	5	666	8.275 295	4
517	7.528 255	8	567	7.794 074	7	617	8.043 891	6	667	8.279 892	5
518	7.533 745	8	568	7.799 219	7	618	8.048 740	6	668	8.284 484	6
519	7.539 227	7	569	7.804 357	6	619	8.053 583	5	669	8.289 070	3
520	7.544 702	7	570	7.809 489	6	620	8.058 421	5	670	8.293 653	6
521	7.550 170	8	571	7.814 615	6	621	8.063 254	6	671	8.298 230	5
522	7.555 630	7	572	7.819 735	6	622	8.068 081	6	672	8.302 802	4
523	7.561 083	7	573	7.824 849	7	623	8.072 902	5	673	8.307 370	5
524	7.566 529	8	574	7.829 956	6	624	8.077 718	5	674	8.311 933	4
525	7.571 967	7	575	7.835 057	7	625	8.082 529	5	675	8.316 492	6
526	7.577 398	7	576	7.840 151	5	626	8.087 335	6	676	8.321 045	4
527	7.582 822	7	577	7.845 240	7	627	8.092 135	6	677	8.325 594	5
528	7.588 239	8	578	7.850 322	6	628	8.096 929	4	678	8.330 138	4
529	7.593 648	7	579	7.855 398	6	629	8.101 719	6	679	8.334 678	5
530	7.599 050	7	580	7.860 468	6	630	8.106 503	6	680	8.339 213	5
531	7.604 445	7	581	7.865 532	7	631	8.111 281	4	681	8.343 743	4
532	7.609 833	8	582	7.870 589	5	632	8.116 055	6	682	8.348 269	6
533	7.615 213	6	583	7.875 641	7	633	8.120 823	5	683	8.352 789	3
534	7.620 587	8	584	7.880 686	5	634	8.125 586	6	684	8.357 306	6
535	7.625 953	6	585	7.885 726	7	635	8.130 343	4	685	8.361 817	4
536	7.631 313	8	586	7.890 759	5	636	8.135 096	6	686	8.366 324	4
537	7.636 665	7	587	7.895 787	7	637	8.139 843	5	687	8.370 827	5
538	7.642 010	6	588	7.900 808	6	638	8.144 585	6	688	8.375 325	5
539	7.647 349	8	589	7.905 823	5	639	8.149 321	4	689	8.379 818	4
540	7.652 680	6	590	7.910 833	7	640	8.154 053	6	690	8.384 307	5
541	7.658 005	8	591	7.915 836	5	641	8.158 779	5	691	8.388 791	4
542	7.663 322	6	592	7.920 834	7	642	8.163 500	5	692	8.393 271	5
543	7.668 633	7	593	7.925 825	5	643	8.168 216	5	693	8.397 746	4
544	7.673 937	8	594	7.930 811	6	644	8.172 927	5	694	8.402 217	5
545	7.679 233	6	595	7.935 791	6	645	8.177 633	5	695	8.406 683	4
546	7.684 523	6	596	7.940 765	6	646	8.182 334	6	696	8.411 145	5
547	7.689 807	8	597	7.945 733	6	647	8.187 029	4	697	8.415 602	4
548	7.695 083	6	598	7.950 695	6	648	8.191 720	6	698	8.420 055	5
549	7.700 353	7	599	7.955 651	5	649	8.196 405	5	699	8.424 503	4
550	7.705 616	7	600	7.960 602	6	650	8.201 085	4	700	8.428 947	5

TABLE 1.

D	$\mu$	D	$\mu$	D	$\mu$	D	$\mu$
700	8.428 947 <sup>4439</sup>	750	8.645 707 <sup>4231</sup>	800	8.852 614 <sup>4046</sup>	850	9.050 708 <sup>3878</sup>
701	8.433 386 <sup>4435</sup>	751	8.649 938 <sup>4227</sup>	801	8.856 660 <sup>4041</sup>	851	9.054 586 <sup>3875</sup>
702	8.437 821 <sup>4431</sup>	752	8.654 165 <sup>4223</sup>	802	8.860 701 <sup>4038</sup>	852	9.058 461 <sup>3872</sup>
703	8.442 252 <sup>4426</sup>	753	8.658 388 <sup>4219</sup>	803	8.864 739 <sup>4035</sup>	853	9.062 333 <sup>3868</sup>
704	8.446 678 <sup>4422</sup>	754	8.662 607 <sup>4216</sup>	804	8.868 774 <sup>4031</sup>	854	9.066 201 <sup>3866</sup>
705	8.451 100 <sup>4418</sup>	755	8.666 823 <sup>4211</sup>	805	8.872 805 <sup>4027</sup>	855	9.070 067 <sup>3863</sup>
706	8.455 518 <sup>4413</sup>	756	8.671 034 <sup>4208</sup>	806	8.876 832 <sup>4025</sup>	856	9.073 930 <sup>3859</sup>
707	8.459 931 <sup>4408</sup>	757	8.675 242 <sup>4203</sup>	807	8.880 857 <sup>4020</sup>	857	9.077 789 <sup>3856</sup>
708	8.464 339 <sup>4405</sup>	758	8.679 445 <sup>4200</sup>	808	8.884 877 <sup>4017</sup>	858	9.081 645 <sup>3853</sup>
709	8.468 744 <sup>4400</sup>	759	8.683 645 <sup>4196</sup>	809	8.888 894 <sup>4014</sup>	859	9.085 498 <sup>3850</sup>
710	8.473 144 <sup>4395</sup>	760	8.687 841 <sup>4192</sup>	810	8.892 908 <sup>4010</sup>	860	9.089 348 <sup>3847</sup>
711	8.477 539 <sup>4392</sup>	761	8.692 032 <sup>4188</sup>	811	8.896 918 <sup>4007</sup>	861	9.093 195 <sup>3844</sup>
712	8.481 931 <sup>4387</sup>	762	8.696 221 <sup>4185</sup>	812	8.900 929 <sup>4004</sup>	862	9.097 039 <sup>3840</sup>
713	8.486 318 <sup>4383</sup>	763	8.700 406 <sup>4180</sup>	813	8.904 929 <sup>4000</sup>	863	9.100 879 <sup>3838</sup>
714	8.490 701 <sup>4378</sup>	764	8.704 586 <sup>4177</sup>	814	8.908 929 <sup>3996</sup>	864	9.104 717 <sup>3834</sup>
715	8.495 079 <sup>4375</sup>	765	8.708 763 <sup>4173</sup>	815	8.912 925 <sup>3993</sup>	865	9.108 551 <sup>3832</sup>
716	8.499 454 <sup>4370</sup>	766	8.712 936 <sup>4169</sup>	816	8.916 918 <sup>3990</sup>	866	9.112 383 <sup>3828</sup>
717	8.503 824 <sup>4365</sup>	767	8.717 105 <sup>4166</sup>	817	8.920 908 <sup>3987</sup>	867	9.116 211 <sup>3825</sup>
718	8.508 189 <sup>4362</sup>	768	8.721 271 <sup>4161</sup>	818	8.924 895 <sup>3983</sup>	868	9.120 036 <sup>3822</sup>
719	8.512 551 <sup>4357</sup>	769	8.725 432 <sup>4158</sup>	819	8.928 878 <sup>3979</sup>	869	9.123 858 <sup>3820</sup>
720	8.516 908 <sup>4353</sup>	770	8.729 590 <sup>4154</sup>	820	8.932 857 <sup>3976</sup>	870	9.127 678 <sup>3816</sup>
721	8.521 261 <sup>4349</sup>	771	8.733 744 <sup>4151</sup>	821	8.936 833 <sup>3973</sup>	871	9.131 494 <sup>3813</sup>
722	8.525 610 <sup>4344</sup>	772	8.737 895 <sup>4146</sup>	822	8.940 806 <sup>3970</sup>	872	9.135 307 <sup>3810</sup>
723	8.529 954 <sup>4341</sup>	773	8.742 041 <sup>4143</sup>	823	8.944 776 <sup>3966</sup>	873	9.139 117 <sup>3807</sup>
724	8.534 295 <sup>4336</sup>	774	8.746 184 <sup>4139</sup>	824	8.948 742 <sup>3963</sup>	874	9.142 924 <sup>3804</sup>
725	8.538 631 <sup>4332</sup>	775	8.750 323 <sup>4136</sup>	825	8.952 705 <sup>3959</sup>	875	9.146 728 <sup>3801</sup>
726	8.542 963 <sup>4328</sup>	776	8.754 459 <sup>4131</sup>	826	8.956 664 <sup>3956</sup>	876	9.150 529 <sup>3798</sup>
727	8.547 291 <sup>4324</sup>	777	8.758 590 <sup>4128</sup>	827	8.960 620 <sup>3953</sup>	877	9.154 327 <sup>3795</sup>
728	8.551 615 <sup>4320</sup>	778	8.762 718 <sup>4125</sup>	828	8.964 573 <sup>3950</sup>	878	9.158 122 <sup>3791</sup>
729	8.555 935 <sup>4315</sup>	779	8.766 843 <sup>4120</sup>	829	8.968 523 <sup>3946</sup>	879	9.161 913 <sup>3789</sup>
730	8.560 250 <sup>4312</sup>	780	8.770 963 <sup>4117</sup>	830	8.972 469 <sup>3943</sup>	880	9.165 702 <sup>3786</sup>
731	8.564 562 <sup>4307</sup>	781	8.775 080 <sup>4114</sup>	831	8.976 412 <sup>3939</sup>	881	9.169 488 <sup>3783</sup>
732	8.568 869 <sup>4303</sup>	782	8.779 194 <sup>4109</sup>	832	8.980 351 <sup>3937</sup>	882	9.173 271 <sup>3780</sup>
733	8.573 172 <sup>4299</sup>	783	8.783 303 <sup>4106</sup>	833	8.984 288 <sup>3933</sup>	883	9.177 051 <sup>3777</sup>
734	8.577 471 <sup>4295</sup>	784	8.787 409 <sup>4103</sup>	834	8.988 221 <sup>3929</sup>	884	9.180 828 <sup>3774</sup>
735	8.581 766 <sup>4291</sup>	785	8.791 512 <sup>4098</sup>	835	8.992 150 <sup>3927</sup>	885	9.184 602 <sup>3771</sup>
736	8.586 057 <sup>4287</sup>	786	8.795 610 <sup>4095</sup>	836	8.996 077 <sup>3923</sup>	886	9.188 373 <sup>3769</sup>
737	8.590 344 <sup>4283</sup>	787	8.799 705 <sup>4092</sup>	837	9.000 000 <sup>3920</sup>	887	9.192 142 <sup>3765</sup>
738	8.594 627 <sup>4278</sup>	788	8.803 797 <sup>4088</sup>	838	9.003 920 <sup>3917</sup>	888	9.195 907 <sup>3762</sup>
739	8.598 905 <sup>4275</sup>	789	8.807 885 <sup>4084</sup>	839	9.007 837 <sup>3913</sup>	889	9.199 669 <sup>3759</sup>
740	8.603 180 <sup>4271</sup>	790	8.811 969 <sup>4080</sup>	840	9.011 750 <sup>3910</sup>	890	9.203 428 <sup>3757</sup>
741	8.607 451 <sup>4266</sup>	791	8.816 049 <sup>4077</sup>	841	9.015 660 <sup>3907</sup>	891	9.207 185 <sup>3753</sup>
742	8.611 717 <sup>4263</sup>	792	8.820 126 <sup>4074</sup>	842	9.019 567 <sup>3904</sup>	892	9.210 938 <sup>3751</sup>
743	8.615 980 <sup>4259</sup>	793	8.824 200 <sup>4070</sup>	843	9.023 471 <sup>3901</sup>	893	9.214 689 <sup>3747</sup>
744	8.620 239 <sup>4254</sup>	794	8.828 270 <sup>4066</sup>	844	9.027 372 <sup>3897</sup>	894	9.218 436 <sup>3745</sup>
745	8.624 493 <sup>4251</sup>	795	8.832 336 <sup>4063</sup>	845	9.031 269 <sup>3894</sup>	895	9.222 181 <sup>3742</sup>
746	8.628 744 <sup>4247</sup>	796	8.836 399 <sup>4059</sup>	846	9.035 163 <sup>3891</sup>	896	9.225 923 <sup>3739</sup>
747	8.632 991 <sup>4243</sup>	797	8.840 458 <sup>4056</sup>	847	9.039 054 <sup>3888</sup>	897	9.229 662 <sup>3736</sup>
748	8.637 234 <sup>4238</sup>	798	8.844 514 <sup>4052</sup>	848	9.042 942 <sup>3884</sup>	898	9.233 398 <sup>3733</sup>
749	8.641 472 <sup>4235</sup>	799	8.848 566 <sup>4048</sup>	849	9.046 826 <sup>3882</sup>	899	9.237 131 <sup>3730</sup>
750	8.645 707	800	8.852 614	850	9.050 708	900	9.240 861

TABLE 1.

D	$\mu$	D	$\mu$
900	9.240 861 <sub>3728</sub>	950	9.423 820 <sub>3590</sub>
901	9.244 589 <sub>3724</sub>	951	9.427 410 <sub>3588</sub>
902	9.248 313 <sub>3722</sub>	952	9.430 998 <sub>3585</sub>
903	9.252 035 <sub>3719</sub>	953	9.434 583 <sub>3582</sub>
904	9.255 754 <sub>3716</sub>	954	9.438 165 <sub>3580</sub>
905	9.259 470 <sub>3713</sub>	955	9.441 745 <sub>3578</sub>
906	9.263 183 <sub>3710</sub>	956	9.445 323 <sub>3574</sub>
907	9.266 893 <sub>3707</sub>	957	9.448 897 <sub>3572</sub>
908	9.270 600 <sub>3705</sub>	958	9.452 469 <sub>3570</sub>
909	9.274 305 <sub>3702</sub>	959	9.456 039 <sub>3567</sub>
910	9.278 007 <sub>3699</sub>	960	9.459 606 <sub>3564</sub>
911	9.281 706 <sub>3696</sub>	961	9.463 170 <sub>3562</sub>
912	9.285 402 <sub>3693</sub>	962	9.466 732 <sub>3559</sub>
913	9.289 095 <sub>3691</sub>	963	9.470 291 <sub>3557</sub>
914	9.292 786 <sub>3687</sub>	964	9.473 848 <sub>3554</sub>
915	9.296 473 <sub>3685</sub>	965	9.477 402 <sub>3552</sub>
916	9.300 158 <sub>3683</sub>	966	9.480 954 <sub>3549</sub>
917	9.303 841 <sub>3679</sub>	967	9.484 503 <sub>3546</sub>
918	9.307 520 <sub>3676</sub>	968	9.488 049 <sub>3544</sub>
919	9.311 196 <sub>3674</sub>	969	9.491 593 <sub>3542</sub>
920	9.314 870 <sub>3671</sub>	970	9.495 135 <sub>3539</sub>
921	9.318 541 <sub>3669</sub>	971	9.498 674 <sub>3536</sub>
922	9.322 210 <sub>3665</sub>	972	9.502 210 <sub>3534</sub>
923	9.325 875 <sub>3663</sub>	973	9.505 744 <sub>3531</sub>
924	9.329 538 <sub>3660</sub>	974	9.509 275 <sub>3529</sub>
925	9.333 198 <sub>3657</sub>	975	9.512 804 <sub>3526</sub>
926	9.336 855 <sub>3655</sub>	976	9.516 330 <sub>3524</sub>
927	9.340 510 <sub>3651</sub>	977	9.519 854 <sub>3521</sub>
928	9.344 161 <sub>3649</sub>	978	9.523 375 <sub>3519</sub>
929	9.347 810 <sub>3647</sub>	979	9.526 894 <sub>3517</sub>
930	9.351 457 <sub>3643</sub>	980	9.530 411 <sub>3514</sub>
931	9.355 100 <sub>3641</sub>	981	9.533 925 <sub>3511</sub>
932	9.358 741 <sub>3639</sub>	982	9.537 436 <sub>3509</sub>
933	9.362 380 <sub>3635</sub>	983	9.540 945 <sub>3506</sub>
934	9.366 015 <sub>3633</sub>	984	9.544 451 <sub>3504</sub>
935	9.369 648 <sub>3630</sub>	985	9.547 955 <sub>3502</sub>
936	9.373 278 <sub>3627</sub>	986	9.551 457 <sub>3499</sub>
937	9.376 905 <sub>3625</sub>	987	9.554 956 <sub>3496</sub>
938	9.380 530 <sub>3622</sub>	988	9.558 452 <sub>3495</sub>
939	9.384 152 <sub>3620</sub>	989	9.561 947 <sub>3491</sub>
940	9.387 772 <sub>3616</sub>	990	9.565 438 <sub>3490</sub>
941	9.391 388 <sub>3615</sub>	991	9.568 928 <sub>3486</sub>
942	9.395 003 <sub>3611</sub>	992	9.572 414 <sub>3485</sub>
943	9.398 614 <sub>3609</sub>	993	9.575 899 <sub>3482</sub>
944	9.402 223 <sub>3606</sub>	994	9.579 381 <sub>3479</sub>
945	9.405 829 <sub>3603</sub>	995	9.582 860 <sub>3477</sub>
946	9.409 432 <sub>3601</sub>	996	9.586 337 <sub>3475</sub>
947	9.413 033 <sub>3598</sub>	997	9.589 812 <sub>3472</sub>
948	9.416 631 <sub>3596</sub>	998	9.593 284 <sub>3470</sub>
949	9.420 227 <sub>3593</sub>	999	9.596 754 <sub>3468</sub>
950	9.423 820	1000	9.600 222

TABLE 2.

$4/D^{1/3}$	R
0.00	0.000 000 0
.01	000 0
.02	000 0
.03	000 0
.04	000 0
0.05	0.000 000 0
.06	000 0
.07	000 0
.08	000 0
.09	000 0
0.10	0.000 000 0
.11	000 1
.12	001 0
.13	001 0
.14	001 1
0.15	0.000 002 0
.16	002 1
.17	003 1
.18	004 1
.19	005 2
0.20	0.000 007 2
.21	009 2
.22	011 3
.23	014 3
.24	017 4
0.25	0.000 021 4
.26	025 5
.27	030 7
.28	037 7
.29	044 8
0.30	0.000 052 9
.31	061 11
.32	072 12
.33	084 13
.34	097 16
0.35	0.000 113 17
.36	130 19
.37	149 22
.38	171 24
.39	195 27
0.40	0.000 222 29
.41	251

When  $D > 1000$  use  
 $\mu = D^{1/3} - 4/D^{1/3} + R$



as it is the one convenient in the other method suggested it was thought desirable to maintain uniformity.

Next is provided in Table 2 a convenient way of dealing with the problem when  $D > 1,000$ . Tartaglia's solution of the cubic equation gives

$$\begin{aligned}\mu &= \left\{ \frac{D}{2} + \frac{D}{2} \left( 1 + \frac{256}{D^2} \right)^{1/2} \right\}^{1/3} + \left\{ \frac{D}{2} - \frac{D}{2} \left( 1 + \frac{256}{D^2} \right)^{1/2} \right\}^{1/3} \\ &= D^{1/3} \left\{ \frac{1}{2} + \frac{1}{2} \left( 1 + \frac{256}{D^2} \right)^{1/2} \right\}^{1/3} + D^{1/3} \left\{ \frac{1}{2} - \frac{1}{2} \left( 1 + \frac{256}{D^2} \right)^{1/2} \right\}^{1/3} \\ &= D^{1/3} - \frac{4}{D^{1/3}} + \frac{2^6}{3} \frac{1}{D^{5/3}} + \frac{2^8}{3} \frac{1}{D^{7/3}} - \frac{2^{14}}{9} \frac{1}{D^{11/3}} - \frac{7 \cdot 2^{14}}{9} \frac{1}{D^{13/3}} + \dots,\end{aligned}$$

where the necessary binomial expansions are easily justified. Now place  $4/D^{1/3} = d$  and write the solution

$$\mu = D^{1/3} - \frac{4}{D^{1/3}} + R,$$

$$\text{where } R = \frac{1}{2^4 \cdot 3} d^5 + \frac{1}{2^6 \cdot 3} d^7 - \frac{1}{2^8 \cdot 3^2} d^{11} - \frac{7}{2^{12} \cdot 3^2} d^{13} + \dots$$

Table 2 gives  $R$  with argument  $4/D^{1/3}$  and the solution is performed for  $D > 1000$  by obtaining  $D^{1/3}$  by linear interpolation in Barlow's tables (Comrie, 1941), then calculating  $4/D^{1/3}$  and finding  $R$  from the table. When  $D > 12,500$ , taking the computer beyond the table of cube roots in Barlow, one of the methods of finding cube roots explained in the introduction to that invaluable work may be used. The table was calculated from the series for  $R$  and the same remarks apply as for Table I except that no subtabulation was done, every value being computed.

For the computation of the other coordinate,  $\lambda$ , in the plane of the orbit  $\mu^2$  is needed. No table of  $\mu^2$  is given since it is quicker to calculate the square of a seven figure number with a machine than to interpolate for it from a table with argument  $D$ .

The constants of the equator are computed for the orbit from the formulae

$$\begin{aligned}A_x &= q\{\cos \omega \cos \Omega - \sin \omega \sin \Omega \cos i\}, \\ B_x &= q\{-\sin \omega \cos \Omega - \cos \omega \sin \Omega \cos i\}, \\ A_y &= q\{(\sin \omega \cos \Omega \cos i + \cos \omega \sin \Omega) \cos \varepsilon - \sin \omega \sin i \sin \varepsilon\}, \\ B_y &= q\{(\cos \omega \cos \Omega \cos i - \sin \omega \sin \Omega) \cos \varepsilon - \cos \omega \sin i \sin \varepsilon\}, \\ A_z &= q\{\sin \omega \sin i \cos \varepsilon + (\sin \omega \cos \Omega \cos i + \cos \omega \sin \Omega) \sin \varepsilon\}, \\ B_z &= q\{\cos \omega \sin i \cos \varepsilon + (\cos \omega \cos \Omega \cos i - \sin \omega \sin \Omega) \sin \varepsilon\},\end{aligned}$$

with the check formula

$$A_x B_x + A_y B_y + A_z B_z = 0.$$

Then having obtained  $\mu$  in one of the above ways the rectangular equatorial heliocentric coordinates  $(x, y, z)$  may be calculated from

$$\begin{aligned}x &= A_x - \frac{A_x}{4} \mu^2 + B_x \mu, \\ y &= A_y - \frac{A_y}{4} \mu^2 + B_y \mu, \\ z &= A_z - \frac{A_z}{4} \mu^2 + B_z \mu.\end{aligned}$$

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# RANK VARIATION IN VITRAIN AND RELATIONS TO THE PHYSICAL NATURE OF ITS CARBONISED PRODUCTS.

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## INTRODUCTION.

The investigations recorded in this paper were carried out with the object of studying variations in the chemical properties of vitrains of all ranks, and also for the purpose of obtaining some fundamental data regarding general relationships between rank of vitrain and the physical nature of products of carbonisation under low-temperature conditions. Vitrain, the purest and most homogeneous of the petrological constituents in coal, was used to obtain comparable results and to avoid the influence of varying proportions of banded constituents which may obscure the significance of results obtained from seam-samples.

The present work on relation between rank of vitrain and physical nature of carbonisation products must be regarded as a preliminary reconnaissance in a wide field of problems where very little fundamental data is available. Carbonisation was carried out under one specific set of conditions, and results represent relationships for those conditions. The nature of cokes and chars depends on many factors such as temperature, rate of heating, pressure on the carbonising mass, and coarseness of the materials before heating. Variation in any of these factors may produce somewhat different results, and a great deal of research is required to elucidate all aspects of the problem. However, it is believed that results, recorded in this paper, have established some general relationships between degree of development of micelle structure in vitrain and the ultra-fine structure of its carbonisation products.

## SELECTION AND PREPARATION OF MATERIAL.

Coals were selected to include as many members of the metamorphic series as possible, from immature peat to anthracite and graphite. The materials range in geological age from Carboniferous to Pleistocene. All important Australian coalfields are represented and materials are included from Great Britain, Germany, Canada, the United States and Antarctica. In the case of coals of sub-bituminous rank or lower, pieces of woody material were selected as the precursors of vitrain, and at the extreme low-rank end of the series a contemporary wood, *Eucalyptus corymbosa*, was included for comparative purposes. Where the coal was of higher rank, specimens containing well-developed vitrain bands were selected, and two or more individual bands, from 0.2 to 0.5 inch in thickness, were separated by hand from each specimen, or from several specimens from the same locality. In the graphitic coal from Rhode Island, U.S.A., the different petrological constituents could not be recognised, and although the coal was used to mark the high-rank extreme of the series, it must be regarded as a *whole coal* sample and not a true vitrain. Fifty-three different coals were selected to provide a complete range in rank. From these, vitrain was carefully separated by hand and granular samples were prepared by crushing, with the minimum production of fines, to pass

through a sieve with circular perforations of 0.06 inch diameter and to be retained on a sieve with perforations of 0.04 inch diameter. Vitrains of sub-bituminous rank or lower (i.e. 79% carbon or less) which undergo permanent moisture changes on drying, were maintained in their original water-saturated condition in all cases where maximum inherent moisture was to be determined. Sieved and graded vitrain from coals of sub-bituminous rank or higher were water-saturated then washed with dilute hydrochloric acid (5% solution) to remove adherent mineral matter, particularly carbonates, deposited in cleat planes. All traces of acid were then washed out, and after setting aside a few grammes of the water-saturated material for determination of maximum inherent moisture, the rest of the sample was air-dried.

#### METHODS OF ANALYSIS AND EXPERIMENTAL TECHNIQUE.

Ultimate and proximate analyses of all samples were carried out by standard technique, using apparatus with slight modifications but generally similar to that described by Himus (1946). Results of analyses are listed in Table 1. Carbon, hydrogen, volatiles and fixed carbon values are quoted on the ash-free, dry basis. Maximum inherent moistures of vitrains and their carbonised products were determined by controlled vaporisation of adherent moisture (Dulhunty, 1947) and results are quoted as percentages, representing grammes of moisture per 100 grammes of dry material. Throughout this paper, all moisture values and references to moisture represent *maximum inherent moisture* which is the total amount of moisture held in the material when all openings, small enough to lower the vapour pressure of water, are filled, and no adherent moisture of normal vapour pressure is present. As described earlier, vitrains separated from coals of sub-bituminous rank or lower were prepared and maintained in their original water-saturated condition to avoid irreversible changes which occur on air drying (Dulhunty, 1948); therefore, maximum inherent moisture values represent a true index of the physical rank of the materials.

A test was designed with the object of studying bulk-volume changes in granular samples of vitrain as a result of carbonisation under free-swelling, low-temperature conditions of heating.

Carbonisation was carried out in an iron tube with an inside diameter of 0.5 inch, and an overall length of 3.2 inches, closed at each end by ground iron plugs. One plug, at the top of the tube, was provided with a central hole of 0.125 inch diameter, for escape of volatiles. A 3.5 inches length of  $\frac{7}{16}$  iron rod was used as a plunger, to measure the depths of vitrain filled into the tube and the residue after carbonisation. The tube, with the lower plug in position, was held vertically and granular vitrain added to a depth of approximately 1.02 inches, measured by inserting the plunger and resting it on the surface of the material which had previously been thoroughly settled down to constant level by gentle tapping. The tube was then heated with the plunger in position, at 110° C. for two hours in an atmosphere of nitrogen, to dry the vitrain. After heating, the plunger was removed and the tube, closed with a cork, was cooled in a stoppered test tube, and the depth of dry vitrain, approximately one inch in all cases, was measured. The plunger was then withdrawn, the upper iron plug inserted, the tube placed in a vertical tube-furnace and heated from room temperature to 600° C. under time-temperature conditions similar to those employed in the Gray King assay. The tube was then removed from the furnace and allowed to cool, after which the iron plug was removed and the depth of carbonised residue measured by inserting the plunger. The difference between measurements before and after carbonisation, representing expansion or contraction, was expressed as a percentage of the depth of dry vitrain originally contained in the tube. Low-temperature carbonisation of all members of the

TABLE I.  
*Properties of Hand Separated Vitrains.*

Spec. No.	Locality.	Geological Age.	Rank.	Per- centage Ash.	Ash-free, Dry Basis.						Percentage Volume Change on Car- bonising.
					At 925° C.		At 600° C.		Per- centage Carbon.	Percentage Hydrogen.	
					Per- centage Vols.	Per- centage F.C.	Per- centage Vols.	Per- centage F.C.			
572	Rhode Island, U.S.A. . .	Carb.	Graphite.	14.1	3.8	96.2	—	—	97.3	2.0	0.0
622	South Wales, Great Britain . .	Carb.	Anthrac.	1.3	5.3	94.7	—	—	93.9	3.6	-2.0
567	Pennsylvania, U.S.A. . .	Carb.	Anthrac.	4.0	5.7	94.3	—	—	93.0	3.7	-1.1
497	Largenbrahm, Ruhr, Ger- many.	Carb.	Anthrac.	0.4	7.0	93.0	—	—	92.7	3.8	-3.3
525	Palmaise, Scotland . .	Carb.	Anthrac.	1.9	6.1	93.9	—	—	92.3	3.5	-4.5
208	Baralaba, Queensland . .	Perm.	Semi-Anthrac.	1.9	10.7	89.3	6.5	93.5	91.6	4.4	-13.1
28	Mittagong, N.S.W. . .	Perm.	Semi-Anthrac.	5.7	7.4	92.6	3.5	96.5	91.5	3.3	-11.1
161	York Plains, Tasmania . .	Trias.	Semi-Anthrac.	3.6	11.7	88.3	7.2	92.8	90.3	3.9	-2.9
36	Currabubula, N.S.W. . .	Perm.	High - rank Bitumin.	22.0	15.7	84.3	—	—	89.2	4.2	-7.1
310	Aberdare, N.S.W. . .	Perm.	High - rank Bitumin.	1.5	39.6	60.4	30.6	69.4	89.2	5.5	+136.0
314	Austinmer, N.S.W. . .	Perm.	High - rank Bitumin.	1.0	27.9	72.1	—	—	88.9	5.2	+598.0
313	Clifton, N.S.W. . .	Perm.	High - rank Bitumin.	0.9	25.5	74.5	16.3	83.7	88.8	4.1	+423.0
30	Balmain, N.S.W. . .	Perm.	High - rank Bitumin.	1.0	23.5	76.5	14.9	85.1	88.3	5.1	+89.0
443	Dapto, N.S.W. . .	Perm.	High - rank Bitumin.	2.5	29.0	71.0	—	—	88.1	5.3	+496.0
312	Helensburgh, N.S.W. . .	Perm.	High - rank Bitumin.	0.8	24.9	75.1	17.8	82.2	88.0	4.7	+476.7
644	Undercliffe, N.S.W. . .	Trias.	High - rank Bitumin.	0.7	36.1	63.9	—	—	85.3	4.9	+524.0
347	Berrima, N.S.W. . .	Perm.	High - rank Bitumin.	3.5	33.3	66.7	—	—	84.8	5.4	+99.1
348	Sydney, N.S.W. . .	Trias.	High - rank Bitumin.	0.8	36.3	63.7	—	—	84.2	5.1	+298.9
646	Sydney, N.S.W. . .	Perm.	High - rank Bitumin.	1.3	33.3	66.7	—	—	84.1	5.3	+60.5
460	Catherine Hill Bay, N.S.W.										

TABLE I.—Continued.  
*Properties of Hand Separated Virrains.*—Continued.

Spec. No.	Locality.	Geological Age.	Rank.	Per- centage Ash.	Ash-free, Dry Basis.							Percentage Volume Change on Car- bonising.
					At 925° C.		At 600° C.		Per- centage Carbon.	Percentage Hydrogen.		
					Per- centage Vols.	Per- centage F.C.	Per- centage Vols.	Per- centage F.C.				
458	Redhead, N.S.W.	Perm.	Med. - rank Bitumin.	2.6	36.9	63.1	—	—	83.7	5.7	+81.0	
459	Belmont, N.S.W. . .	Perm.	Med. - rank Bitumin.	1.8	37.6	62.4	—	—	83.4	5.4	+21.0	
288	Wonthaggi, Victoria	Jur.	Med. - rank Bitumin.	1.2	34.4	65.6	24.9	75.1	82.0	5.2	0.0	
124	Mt. Nicholas, Tasmania . .	Trias.	Med. - rank Bitumin.	0.4	34.6	65.4	18.1	81.9	81.9	5.1	—4.0	
169	Wallsend, N.S.W.	Perm.	Med. - rank Bitumin.	2.1	34.4	65.6	26.4	73.6	81.3	5.0	+2.0	
174	Liddell, N.S.W. . .	Perm.	Med. - rank Bitumin.	3.0	40.9	59.1	31.5	68.5	81.0	6.8	+58.8	
172	Rix Creek, N.S.W.	Perm.	Med. - rank Bitumin.	0.4	38.9	61.1	25.9	74.1	80.9	5.1	+49.0	
181	Kandos, N.S.W.	Perm.	Med. - rank Bitumin.	0.6	36.3	63.7	27.6	72.4	80.8	5.1	+46.0	
212	Mt. Mulligan, Queensland	Perm.	Med. - rank Bitumin.	1.6	29.7	70.3	19.9	80.1	80.7	4.8	—11.9	
138	Wonthaggi, Victoria	Jur.	Med. - rank Bitumin.	1.0	38.2	61.8	27.8	72.2	80.3	4.9	+2.1	
186	Seymour, Tasmania	Trias.	Low - rank Bitumin.	2.7	36.5	63.5	27.0	73.0	80.0	5.0	—12.8	
461	Swansea, N.S.W.	Perm.	Low - rank Bitumin.	6.5	36.3	63.7	—	—	79.8	5.2	+7.6	
143	Ipswich, Queensland.	Trias.	Low - rank Bitumin.	5.0	35.5	64.5	26.1	73.9	79.1	5.2	+2.8	
209	Callide, Queensland	Jur.	Sub-Bitumin.	1.8	36.8	63.2	26.6	73.4	77.9	4.8	—24.7	
317	Collie, Western Australia	Perm.	Sub-Bitumin.	2.4	32.9	67.1	—	—	76.6	5.9	—	
120	Collie, Western Australia	Perm.	Sub-Bitumin.	1.9	34.7	65.3	29.7	70.3	74.8	4.9	—24.5	
304	Leigh Creek, South Australia	Trias.	High - rank Brown Coal.	3.8	36.2	65.8	30.6	69.4	74.5	4.5	—22.4	

TABLE I.—Continued.  
Properties of Hand Separated Vitreins.—Continued.

Spec. No.	Locality.	Geological Age.	Rank.	Per- centage Ash.	Ash-free, Dry Basis.						Percentage Volume Change on Car- bonising.
					At 925° C.		At 600° C.		Per- centage Carbon.	Percentage Hydrogen.	
					Per- centage Vols.	Per- centage F.C.	Per- centage Vols.	Per- centage F.C.			
296	Benwerrin, Victoria	Tert.	High - rank Brown Coal.	2.5	36.5	63.5	30.3	69.7	72.9	4.4	—25.0
290- 291	Leigh Creek, South Australia	Trias.	High - rank Brown Coal.	6.5	41.9	58.1	34.5	65.5	71.9	4.5	—23.2
456	Moosonee, Canada	Cret.	Med. - rank Brown Coal.	2.7	51.6	48.4	—	—	69.8	5.4	—42.2
457	Bovey Tracey, England	Tert.	Med - rank. Brown Coal.	1.9	54.4	45.6	—	—	69.6	5.6	—40.5
88	Berridale, N.S.W.	Tert.	Med. - rank Brown Coal.	3.2	53.8	46.2	38.4	61.6	68.9	5.5	—28.5
299	Yallourn, Victoria	Tert.	Med. - rank Brown Coal.	1.1	52.4	47.6	43.0	57.0	68.4	5.4	—23.7
454	Liblar, Germany	Tert.	Med. - rank Brown Coal.	1.4	54.7	45.3	—	—	68.3	5.5	—51.6
286	Bacchus Marsh, Victoria	Tert.	Med. - rank Brown Coal.	4.5	50.3	49.7	42.7	57.3	68.0	5.1	—25.9
136	Yallourn, Victoria	Tert.	Med. - rank Brown Coal.	1.8	60.1	39.9	41.8	58.2	67.4	4.3	—24.5
142	Kiandra, N.S.W.	Tert.	Low - rank Brown Coal.	0.6	62.0	38.0	51.7	48.3	66.3	6.1	—28.7
298	Kerguelen Island, Ant- arctica.	Tert.	Low - rank Brown Coal.	7.1	52.5	47.5	44.2	55.8	63.8	5.1	—23.0
283	Kelso, Tasmania	Mioc.	Low - rank Brown Coal.	0.5	55.3	44.7	45.3	54.7	63.4	5.1	—33.7
455	Cologne, Germany	Tert.	Low - rank Brown Coal.	1.8	64.6	35.4	—	—	62.5	5.9	—50.1
104	Kiandra, N.S.W.	Tert.	Low - rank Brown Coal.	0.4	76.4	23.6	62.8	37.2	59.2	6.1	—21.6
453	Haltern, Germany	Tert.	Peat.	0.3	87.7	12.3	—	—	58.4	7.3	—66.0
282	<i>Euc. corymbosa</i> , Victoria	Contemp.	—	0.1	82.1	17.9	72.6	27.4	52.1	5.6	—38.8
75	Potts Point, N.S.W.	Pleist.	Peat.	5.1	75.0	25.0	69.7	30.3	51.3	5.7	—31.6

series was carried out, and results (see Table 1) recorded as positive values where expansion took place, and negative values where contraction occurred.

Results with a high degree of reproducibility were obtained for the materials which underwent contraction, and also for most of those which showed expansion. However, some difficulty was experienced with vitrain of maximum swelling properties, as expansion was so great in some cases that the tube was of insufficient length to accommodate the coke. For these vitrains, which contained 85% to 88% carbon and gave expansions of more than 100%, a depth of 0.3 inch of the granular material was filled into the tube before carbonisation, enabling expansion results to be obtained. This introduced a variation in the conditions of carbonisation for a limited number of the strongly swelling vitrains, but their expansion was so great compared with all other members of the metamorphic series that discrepancies due to varied experimental conditions could not materially influence the general significance of results obtained.

After each test, the carbonised product was carefully removed from the tube and observations made as to its character. It was then crushed, where necessary, and sieved and graded as described earlier in the preparations of the vitrains. Some interesting features were noted in comparing the general nature of the granular samples of the vitrains with that of their carbonised products, and these observations are described later in this paper.

The residues from the carbonisation tests were saturated in preparation for determination of maximum inherent moisture, by boiling the granular material in water under reflux for one hour and then allowing it to stand in air-free water, in a tightly sealed test tube, for at least four days. Maximum inherent moisture was then determined in the same way as for the saturated vitrains. Behaviour of the carbonised products during removal of adherent moisture was exactly similar to that of the vitrains, except for cokes of strongly swelling vitrains which took a longer time to reach apparent dryness. Results for moisture determinations of the carbonised products (see Table 2) could be reproduced with the same degree of accuracy as those obtained for vitrains.

#### NOTES ON CHEMICAL PROPERTIES OF VITRAINS.

The selected materials range in carbon from 51.3% for a Pleistocene peat to 97.3% for the Rhode Island anthracite: the highest carbon determined for an Australian vitrain being 91.5%, which was obtained for a semi-anthracite from Mittagong, N.S.W. In this instance, anthracitisation is directly attributable to local igneous alteration by a sill. In general, there is a notable lack of true anthracite coals in Australian coalfields, due to the absence of widespread igneous alteration or folding of the Permian coal measures.

Hydrogen values obtained for the complete series vary between limits of 2.0% and 7.3%. Raistrick and Marshall found that a series of vitrains from American coals ranged from 5.1% to 6.0% hydrogen. Their materials, varying from 55% to 90% carbon, were all from American coalfields, whereas materials used in the present work came from widely scattered areas in different countries.

In a more detailed study of the constitution of vitrains from American coals, Marshall (1943) obtained results which present an interesting comparison with hydrogen values obtained for Australian vitrains. For the American series with a variation of 55.6% to 87.8% carbon it was found that hydrogen varied within limits of 4.6% and 6.0%. These figures were obtained from analyses of sixty-six samples of vitrain and it was noted that 95.5% of all members of the series had a hydrogen content between 5% and 6%. Hydrogen determined for Australian vitrains in the present investigation varies between limits of 4.4% and 6.8% for a similar carbon range (51.3% to 88.0%). This group contains thirty-four different samples but only 61.8% of these vitrains had a



hydrogen content between 5% and 6%; that is, a little more than half of the materials conformed to the variation determined by Marshall. Of the remainder, 29.4% had a hydrogen content of less than 5%, and the rest (8.8% of the series) had more than 6% hydrogen. Considering hydrogen content of Australian vitrains of all ranks, from 51.3% to 91.6% carbon, limits of hydrogen range from 3.3% to 6.8%, with only 58% of the vitrains analysed having a hydrogen content between 5% and 6%; from which it would appear that the proportion of hydrogen in Australian vitrains may vary over a considerably wider range of values than that determined for American vitrains. This contrast in proportions of hydrogen in vitrains from coals of the Northern and Southern Hemispheres may be the result of different environmental conditions of coalification or it may indicate fundamental differences in the nature of the original coal-forming constituents. It suggests that the plant material from which Australian coals were derived was of greater, or different, variety to that which gave rise to the American coals.

Standard proximate analyses at 925° C. (see Table 1) of all members of the vitrain series confirms the well-established continuous variation of volatile content with rank. Actual values range from a minimum of 3.8% for the Rhode Island material to a maximum of 87.7% for a German peat. Volatile yields calculated from low-temperature carbonisation of a selected number of the vitrains shows the same general increase in volatiles with increase in rank. However, actual values obtained for volatiles were much lower at the lower temperature. In plotting volatiles at 925° C. and at 600° C. against carbon, two distinct zones are obtained, the volatiles determined at the higher temperature falling in the upper zone. An examination of the differences in volatile contents obtained at the different temperatures shows that the increase in values at the higher temperature is not constant, and has no relationship to the rank of the vitrain from which it was obtained. Actual increases vary between limits of 3.9 and 18.3%.

Ash values for the vitrains are generally low, ranging from 0.1% to 6.0% with an overall average of 2.8% for the whole series; exceptions are the high ash values obtained for the Rhode Island anthracite and the Currabubula (N.S.W.) material, neither of which, however, was included in the preliminary acid washings. The anthracite, as already mentioned, cannot be regarded as a pure vitrain and the Currabubula material came from an area closely associated with igneous intrusion, producing an exceptionally high-ash coal.

#### NATURE OF THE CARBONISED PRODUCTS.

The carbonised residues of the granular vitrains fall into two distinct groups, which for the purpose of this paper will be referred to as *chars* and *cokes*. The chars are the non-coherent residues and the cokes are the coherent residues. Since all members of the metamorphic series are represented the nature of the carbonised residues varies considerably. Cokes are formed from vitrains of 79% to 89% carbon. Where carbon of the vitrain lies between 83% and 89%, a completely fused coke is formed in which no trace remains of the original individual grains. Two types of completely fused coke are recognisable and are described as *bubbly fused coke* and *dense fused coke*. The former is a coarsely porous or intumesced coke and the latter is more finely porous and rather compact. Their formation does not seem to depend on the carbon content within this particular carbon range, nor does it seem to be related to the actual percentage of volatiles. However, the formation of bubbly fused coke is directly related to bulk-volume changes on carbonisation and is probably associated with the plastic properties of the vitrain during thermal decomposition.

Where the carbon of the vitrain ranges between 79% and 83%, the form of the carbonised residue varies greatly, this being in the nature of a transition

zone between the chars and the cokes, both of which are represented. Cokes of this group are typically partly fused or granular with the original grains distinguishable though they have become rounded or globular. Two types of granular cokes are distinguished and described as *strongly coherent granular coke* and *weakly coherent granular coke*, the distinction, as the terms suggest, being based on the degree of coherency of the individual grains.

Chars are formed from vitrains of both higher and lower rank than those which produce cokes. The chars formed from vitrains of sub-bituminous or lower rank (i.e. 79% carbon or less) will be referred to as *low-rank chars*, and those formed from vitrains on the high-rank, or anthracite, side of the coking vitrains (i.e. higher than 89.2% carbon) will be termed *high-rank chars*. Both low-rank and high-rank chars are completely non-coherent but it will be seen later that they are further distinguished by differences in their ultra-fine structure. It was noted that chars formed from vitrains which were originally bright have a brighter lustre than the vitrains from which they were formed. This was observed in chars from vitrains of both sub-bituminous and anthracite rank. However, vitrains from the brown coals and peats, which are dull in their original water-saturated condition and vary in colour from brown to black, form dull, black chars.

#### RELATION OF BULK-VOLUME CHANGES ON CARBONISATION TO RANK.

Results of bulk-volume changes on low-temperature carbonisations of granular vitrain, under free-swelling conditions as described earlier in this paper, are recorded in Table 1. Values obtained for percentage expansion or contraction were plotted against carbon as rank index, as illustrated in Figure 1. All points on the graph fall within a zone of fairly constant width, with a maximum in the region of the coking coals. The relationship so obtained illustrates variation in bulk-volume changes with rank. Where carbon of the vitrain is less than 79%, or exceeds 89%, contraction in bulk-volume takes place, with the formation of a char. Between 79% and 83% carbon, either contraction or expansion may take place, and where carbon lies between 83% and 89% expansion only is obtained.

On the low-rank side of the graph there is a suggestion of a zonal minimum in the region of 67% carbon. This corresponds very closely with the maximum in the moisture-rank relationship recorded by Dulhunty (1948) for the same vitrains, and it is suggested by that author that the maximum in moisture probably corresponds with the maximum degree of colloidal development attained during coalification. However, while the zonal maximum (Fig. 1) corresponds approximately with maximum colloidal development in the vitrain, the greatest contraction recorded (Vitrain No. 453) falls towards the low-rank side of the zonal minimum. This vitrain, having a contraction of 66%, is a peat wood from Haltern, Germany. It is perhaps significant that it undergoes least irreversible change on drying, and that maximum irreversible changes on drying are recorded (Dulhunty, 1948) for those materials falling in the region of the zonal minimum.

Vitrains of carbon content between 83% and 89% all show expansion on carbonisation, and the peak of this section of the zone lies at approximately 86% carbon. Expansion for these materials ranges from 21% to 598%, and the carbonised residues are all completely fused. There would seem to be some relationship between degree of expansion and maximum inherent moisture of the original vitrain. That the coking coals corresponded with the minimum in the moisture-carbon curve has long been recognised and more recently illustrated by Dulhunty (1948). From the results recorded in this paper (Fig. 1), it may be noted that for points lying towards the maximum of the expansion-carbon zone, where expansion values exceed 300%, moisture of the vitrains is

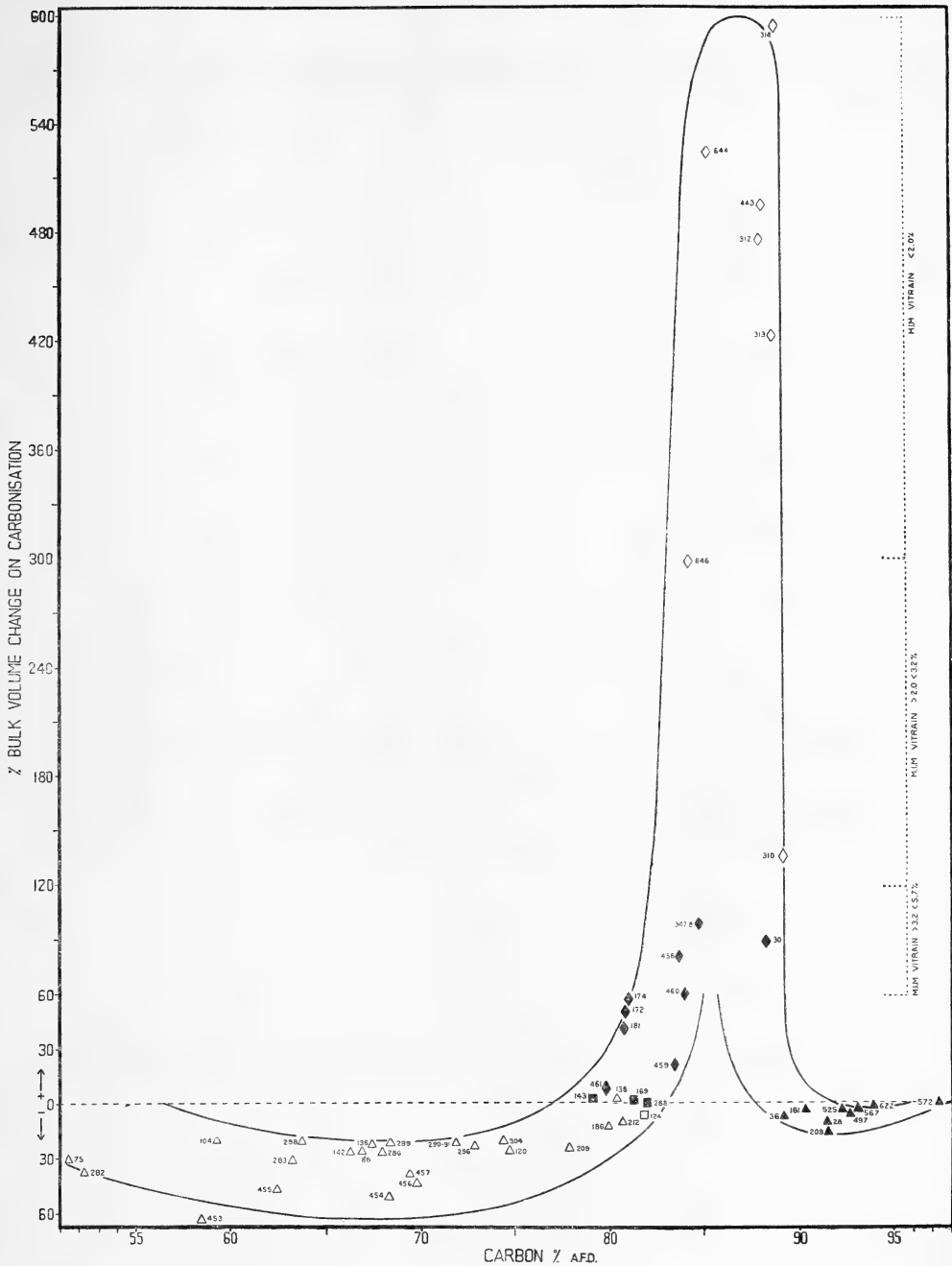


Fig. 1.—Relation of Rank to Bulk-Volume Changes on Carbonisation.

(For key to symbols see Fig. 2.)

2% or less. Where expansion exceeds 120% but not 300%, moisture values lie between 2% and 3.2%, and where expansion is greater than 60% but does not exceed 120%, moisture ranges between 3.2% and 5.7%. At the same

time, vitrains for which expansion values exceed 120% form bubbly fused cokes, and where expansion lies between 60% and 120%, dense fused cokes are formed.

In the 79% to 83% carbon group, where both expansion and contraction values are recorded, the carbonised residues are of various types. One vitrain (No. 288) of this group exhibits no change in bulk-volume on carbonisation. In this particular instance, tendencies to contract or expand are apparently compensating, although considerable changes occur in the ultra-fine structure of the material as will be illustrated later in this paper. Similar properties on carbonisation are also exhibited by the graphitic material, No. 572.

Considering again the chars formed from vitrains on both the high-rank and low-rank sides of the coking vitrains it was noted that in the case of the low-rank chars contraction in every instance exceeded 15%, while for the high-rank chars contraction did not exceed 15%.

In experiments designed to test the relation of free-swelling index to expansion of coal in experimental coke ovens for a series of coals ranging from low-volatile to high-volatile bituminous in rank, Selvig and Ode (1946) recorded measurements of percentage contraction and expansion on carbonisation. However, it was not possible to correlate their work with results obtained from vitrains of this series of similar rank, as materials used were pulverised rather than granular, and temperature ranges were not recorded for the experiments.

Cannon, Griffith and Hirst (1943) in their work on carbonisation of coals, also recorded measurements of contraction and expansion obtained on carbonising powdered coal which they related to heat of wetting phenomena. However, conditions of carbonisation were not comparable with those used in this work: time-temperature conditions were similar, but pulverised coal was used rather than granular vitrain and expansion and contraction measurements were not obtained under free-swelling conditions.

#### CHANGES IN PORE STRUCTURE IN VITRAIN ON CARBONISATION AND RELATION TO RANK.

As described earlier in this paper, maximum inherent moisture determinations were carried out on the carbonised residues of all vitrains in the series (see Table 2). In the case of vitrain, maximum inherent moisture depends on the natural condition of the micelle structure determined by metamorphic evolution in the earth's crust. Maximum inherent moisture of the carbonised product depends on the effects of carbonisation, but in each case it is presumably a measure of something closely related to the total volume of openings forming part of the ultra-fine structure, and small enough to lower the vapour pressure of water.

No definite relationship was established between maximum inherent moisture of the carbonised product and carbon of the vitrain from which it was formed. In many instances the moisture in the carbonised residue exceeded that of the corresponding vitrain, and in other instances was lower. It was found, however, that the difference between the moisture of vitrain and its carbonisation products is closely related to carbon content, or rank, of the vitrain. To illustrate this, the numerical difference between the moisture values for the vitrain and its carbonised product was expressed as a percentage of the moisture of the vitrain. Where moisture of the carbonised residue exceeded that of the vitrain, the increase was expressed as a positive value, and conversely, a decrease was expressed as a negative value (see Table 2). This percentage increase or decrease in moisture was then plotted against carbon determined for the original vitrain. A well-defined zonal relationship was established (see Fig. 2), the form of the zone being illustrated by lines

TABLE 2.  
*Maximum Inherent Moisture of Vitrains and Their Carbonisation Products.*

Spec. No.	Percentage Carbon A.F.D. Basis.	Percentage Maximum Inherent Moisture. Dry Basis.		Actual Actual Difference.	Percentage Increase or Decrease.
		Vitrain.	Carbonised Product.		
572	97.3	3.5	4.0	+0.5	+14.3
622	93.9	5.1	4.6	-0.5	-9.8
567	93.0	4.1	4.8	+0.7	+17.1
497	92.7	2.3	4.6	+2.3	+100.0
525	92.3	4.7	6.1	+1.4	+29.8
208	91.6	3.2	6.8	+3.6	+112.5
28	91.5	3.7	4.7	+1.0	+27.0
161	90.3	3.9	6.2	+2.3	+59.0
36	89.2	5.9	6.9	+1.0	+17.0
310	89.2	3.9	13.1	+9.2	+235.9
314	88.9	2.0	4.7	+2.7	+135.0
313	88.8	1.8	4.7	+2.9	+161.0
30	88.3	3.2	29.8	+26.6	+831.3
443	88.1	1.9	5.7	+3.8	+200.0
312	88.0	1.8	6.8	+5.0	+277.7
644	85.3	2.0	5.5	+3.5	+175.0
347-348	84.8	3.9	4.2	+0.3	+7.7
646	84.2	2.6	5.7	+3.1	+119.2
460	84.1	5.7	10.4	+4.7	+82.5
458	83.7	3.9	6.0	+2.1	+53.8
459	83.4	4.7	12.8	+8.1	+172.3
288	82.0	12.8	35.9	+23.1	+180.5
124	81.9	18.2	16.2	-2.0	-11.0
169	81.3	5.4	17.5	+12.1	+224.1
174	81.0	3.9	14.5	+10.6	+271.8
172	80.9	6.0	35.3	+29.3	+488.3
181	80.8	6.4	36.6	+30.2	+471.9
212	80.7	6.8	7.3	+0.5	+7.4
138	80.3	15.3	25.8	+10.5	+68.6
186	80.0	9.9	19.1	+9.2	+93.0
461	79.8	5.7	6.7	+1.0	+17.5
143	79.1	4.3	33.5	+29.2	+680.0
209	77.9	21.1	8.6	-12.5	-59.2
317	76.6	25.4	9.7	-15.7	-61.8
120	74.8	25.5	9.5	-16.0	-62.8
304	74.5	64.9	12.7	-52.2	-80.4
456	69.8	82.8	11.7	-71.1	-85.9
457	70.5	60.3	14.0	-46.3	-76.8
88	68.9	76.3	16.6	-59.7	-78.4
454	68.3	93.3	10.5	-82.8	-88.7
136	67.4	116.0	15.3	-100.7	-86.8
455	62.5	68.0	10.1	-57.9	-85.2
104	59.2	61.0	21.6	-39.4	-64.6
453	58.4	38.6	24.2	-14.4	-37.3

drawn at the approximate margins of the areas occupied by the points on the graph. This zone represents relationship of rank to moisture change on carbonisation.

All low-rank materials, that is vitrain of 79% carbon or less, show a decrease in moisture on carbonisation. At the low-rank extreme, a decrease in moisture of 37.3% is recorded for a peat wood of 58.4% carbon. As rank increases, the percentage decrease in moisture becomes greater till a zonal minimum is reached

at approximately 68% carbon. With further increase in rank the zone gradually rises, and at 79% carbon it becomes almost vertical, and all vitrains at this rank or higher show, with two minor exceptions, an increase in moisture on carbonisation. Between approximately 79% and 90% carbon there is a well-defined maximum, the peak of which is probably situated at about 86% carbon. Where carbon lies between 79% and 82%, that is, for vitrains of bituminous rank, the increase in moisture may be as much as 832%, or as little as 7.4%. A sharp reduction in moisture increase occurs at 90% carbon, and towards the anthracite end of the zone, increase in moisture does not exceed 115% and gradually lessens as carbon approaches 100%.

An interesting comparison may be made in the form of this zone and that obtained by Dulhunty (1948) for the maximum inherent moisture-carbon relationship of the same vitrains. The maximum in the moisture-carbon curve at 68% carbon, corresponds exactly with the zonal minimum in the relationship of rank to moisture change on carbonisation. However, the apparent peak, at 86% carbon, of the zonal maximum in this relationship (Fig. 2) is a little to the low-rank side of the minimum in the moisture-carbon curve which falls at about 88% carbon.

The zonal relationship of rank to moisture change on carbonisation is closely allied in form to that established for the relationship of bulk-volume change on carbonisation to rank (Fig. 1). In both instances zonal minima are established at 68% carbon and the peaks of the maxima are developed at 86% carbon approximately. Vitrains of 79% carbon and less show a decrease in moisture on carbonisation and a contraction in bulk-volume. Between 79% and 83% carbon, with one exception, all materials show an increase in moisture, but changes in bulk-volume may be either contraction or expansion. Where vitrains are of coking bituminous rank, that is, between 83% and 89% carbon, maximum expansion is recorded and all vitrains of this group show an increase in moisture on carbonisation. An interesting feature in the comparison of these relationships is the increase in moisture in vitrains of 89% carbon or more all of which suffer contraction in bulk-volume on carbonisation.

Earlier in this paper a distinction is drawn between low-rank and high-rank chars. The relationship of moisture change on carbonisation to rank shows that a further distinction may be drawn on the basis of properties related to the ultra-fine structure of the chars. The carbonised residues of low-rank vitrains all show a decrease in moisture exceeding 37%, while the high-rank chars, with one exception, show an increase in moisture. An increase in moisture on carbonisation is also shown by any vitrain which produces a completely fused coke. From the illustration in Fig. 2 it will be seen that the greatest increase in moisture is obtained for dense fused cokes, and not for bubbly fused cokes which emphasizes that the bubbly structure is a macroscopic feature.

It is interesting and perhaps significant to note that the formation of low-rank chars is accompanied by a decrease in maximum inherent moisture whilst the formation of high-rank chars involves an increase. The plastic properties of coking coals during carbonisation have long been recognised and in vitrain undergoing plastic deformation it is not difficult to visualise the necessary rearrangement of the ultra-fine structure required to give an increase in moisture on carbonisation. Yet moisture increases are obtained in the case of the high-rank vitrains which do not undergo plastic deformation in the same way, but produce a char in which the identity of the original individual particles is retained.

From the study of heat of wetting and carbonisation, carried out by the British Coal Utilisation Research Association (Cannon, Griffith and Hirst, 1943) on coals varying in rank from high volatile bituminous through to medium volatile anthracites, it was concluded that the micelle structure, or something related to it, persists throughout carbonisation. It was also concluded that

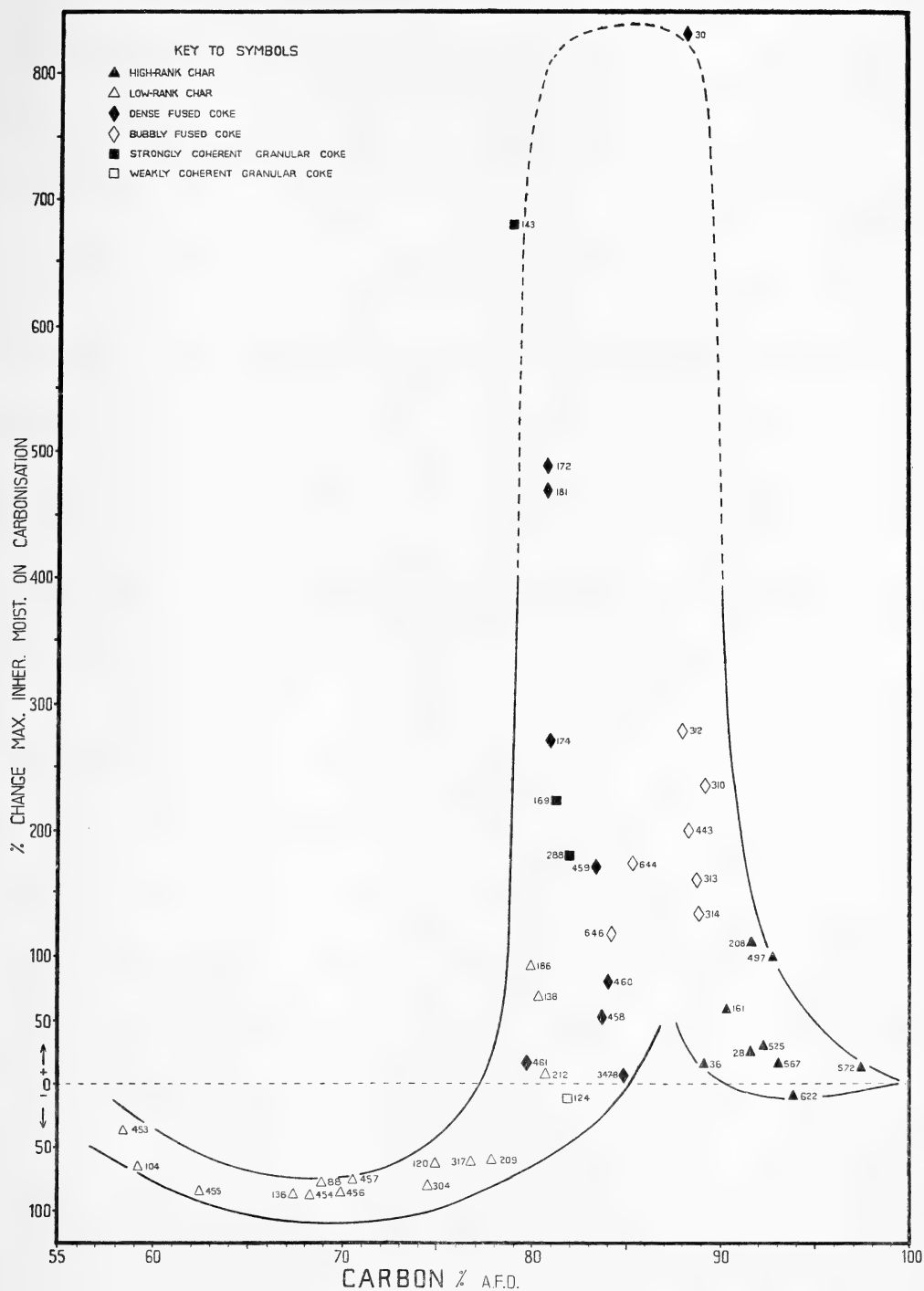


Fig. 2.—Relation of Rank to Per Cent. Change in Maximum Inherent Moisture on Carbonisation.

there is no great change in the internal surface area in so much that coals of small surface give carbonised products of small surface, and those with large surface give carbonisation products with large internal surface.

In so far as maximum inherent moisture determinations may be considered a measure of total internal volume of the coal substance (King and Wilkins 1943), then broadly the effects of carbonisation on the internal volume of the vitrains are as follows :

- (1) Volume decreases if the vitrain contains less than 79% carbon, or more significantly perhaps, if the material has not attained that critical stage in the process of coalification (Dulhunty, 1948) beyond which irreversible changes on drying do not take place.
- (2) Volume increases where carbon of the vitrain exceeds 79%, i.e. vitrain coalified beyond the stage at which irreversible changes take place on drying.

In the first case, carbonisation of the low-rank coals is accompanied by considerable loss of substance due to devolatilisation, and materials of this rank do not undergo plastic deformation during the process of carbonisation which produces a char. Reduction in internal volume then may be satisfactorily accounted for by the increased areas of contact between the micelle (with corresponding decrease in inter-micelle spaces) as suggested by Bangham (1943) and Bangham and Maggs (1943) to be the result of carbonisation. At the same time, these vitrains suffer a decrease in bulk-volume under free-swelling conditions of carbonisation.

The second group includes both the coking vitrains and those which give high-rank chars. The former give very great increases in internal volume, particularly vitrains from which dense fused cokes are formed. If, as heat of wetting determinations, carried out at various stages during the carbonisation of bituminous and anthracitic coals, and electrical conductivity measurements, would seem to so clearly indicate, the micelle structure or something related to it persists throughout carbonisation, it is difficult to account for the very large increases in internal volume recorded here for vitrains of similar rank and carbonised under similar conditions. The suggestion is offered that a new or supplementary pore structure is developed, dependent on the nature and rate of evolution of the volatiles and the degree of plasticity during carbonisation. In this structure the pores may be of such dimensions as to be inaccessible to the methanol molecule used in heat of wetting-surface area determinations, but accessible to the smaller water molecule used to measure internal volume. Alternatively, it is suggested that the original pore structure almost entirely disappears, being replaced by pores of greater radii which would increase internal volume but not internal area. That such a structure could result from gaseous emanations through a plastic medium during carbonisation is a possibility for consideration in the case of the coking vitrains, or those exhibiting intumescence, but it does not satisfactorily account for increases in internal volume obtained for vitrains producing high-rank chars. The latter do not undergo plastic deformation during carbonisation and volatile evolution is relatively insignificant; moreover, a decrease in *bulk-volume* accompanies an increase in *internal volume* for the high-rank chars. The elucidation of these apparent anomalies offers an interesting problem for further research.

#### ACKNOWLEDGEMENTS.

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#### SUMMARY.

Vitrains of all ranks from the Southern Hemisphere show greater variation in hydrogen content than those from the Northern Hemisphere, suggesting differences in original plant materials. Volatile yields at 920° C. exceed those at 600° C. by a variable amount which cannot be related to rank. A zonal relationship exists between rank and bulk-volume changes on carbonisation with a minimum at 67% carbon and a maximum at 86% carbon. A similar relationship was established between rank and differences in capillary-held moisture of vitrain and its carbonisation products. These relationships indicate that vitrains of 79% carbon or less produce chars, or non-coherent residues, showing an overall contraction in bulk-volume exceeding 15% and holding less capillary-condensed moisture than the original vitrain. Where carbon of the vitrain is 79% and does not exceed 89·2%, a coke is formed which may show either contraction or expansion in bulk-volume but in which capillary-condensed moisture exceeds that of the original vitrain. A char is also formed from vitrains of 89·2% carbon or more, in which overall contraction in bulk-volume does not exceed 15% and in which the amount of capillary-condensed moisture exceeds that of the original vitrain.

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# THE AUSTRALIAN SOCIAL SERVICES CONTRIBUTION AND INCOME TAX ACTS, 1949.

By H. MULHALL.

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## I.

Professor H. S. Carslaw has examined in a series of papers the graduation of Australian taxation on individual incomes from the introduction of uniform taxation in 1942 to the Social Services Contribution and Income Tax Acts of 1947 which were relevant to the year ending June 30th, 1948. Since the appearance of his last paper (Carslaw, 1948) there have been two further reductions in taxation. It is now proposed to set out for the most recent Act the analysis given by Professor Carslaw for the Act of 1947. His notation is retained; the amount of tax and/or contribution on an income of £x is denoted by T pence.

The rate of tax on this income is denoted by  $R\left(=\frac{T}{x}\right)$  with, if required, a suffix,

say  $R_1$  or  $R_2$ . The rebatable amount on the income is denoted by £A.

## II.

The basic rate of contribution applying to a taxpayer entitled to no rebates is given by the formula

$$R_1 = 3 + \frac{3}{80}(x - 100), \text{ when } x \leq 500.$$

The maximum rate of 18 pence is reached at  $x = 500$ .

The amount of contribution payable is thus

$$T = x \left[ 3 + \frac{3}{80}(x - 100) \right].$$

The contribution commences at  $x = 105$ , but there is a proviso that no person shall pay a contribution greater than half the excess of his income over £104.

For taxpayers entitled to rebates on account of dependents, medical expenses, etc., the concessional rate is given by the formulæ

$$\begin{aligned}
 R_2 &= \frac{3x-A}{100} \text{ when } x-A < 100 \\
 &= 3 + \frac{3}{80}(x-A-100) \text{ when } 100 \leq x-A < 500. \\
 &= 18 \text{ when } x-A \geq 500.
 \end{aligned}$$

When using these formulæ it should be noted that there is a special rebate for a taxpayer whose income does not exceed £350 and who has any dependents. This rebate is £50 when the income does not exceed £250, diminishing by £1 for every £2 by which the income exceeds £250, so that it vanishes at £350.

The following list shows the incomes at which liability to Social Services Contribution begins and those at which the maximum rate of 18 pence in the £ is reached.

	£
Single person .. .. .	105-500
Person with dependent wife .. .. .	201-650
Person with dependent wife and one child .. .. .	284-750
Person with dependent wife and two children .. .. .	318-800
Person with dependent wife and three children .. .. .	351-850
Person with dependent wife and four children .. .. .	401-900
Person with dependent wife and five children .. .. .	451-950

### III.

This section deals with Income Tax as distinct from Social Services Contribution, which must, of course, be added to the amounts calculated from the formulæ which follow to give the total amount payable. The formulæ refer to taxpayers entitled to no rebates.

#### *Earned Income.*

(a) When  $x \leq 500$ ,  
 $T=0$ .

(b) When  $500 < x \leq 1000$ ,  

$$\begin{aligned}
 T &= (x-500) \left[ 18 + \frac{24}{1000}(x-500) \right] \\
 &= \frac{24}{1000}x^2 - 6x - 3000.
 \end{aligned}$$

(c) When  $1000 < x \leq 2000$ ,  

$$\begin{aligned}
 T &= 15 \times 1000 + (x-1000) \left[ 42 + \frac{2}{100}(x-1000) \right] \\
 &= \frac{2}{100}x^2 + 2x - 7000.
 \end{aligned}$$

(d) When  $2000 < x \leq 5000$ ,  

$$\begin{aligned}
 T &= 38.5 \times 2000 + (x-2000) \left[ 82 + \frac{1}{100}(x-2000) \right] \\
 &= \frac{1}{100}x^2 + 42x - 47000.
 \end{aligned}$$

(e) When  $5000 < x \leq 10,000$ ,

$$\begin{aligned} T &= 82 \cdot 6 \times 5000 + (x - 5000) \left[ 142 + \frac{2}{1000}(x - 5000) \right] \\ &= \frac{2}{1000}x^2 + 122x - 247,000. \end{aligned}$$

(f) When  $x > 10,000$ ,

$$T = 117 \cdot 3 \times 10,000 + 162(x - 10,000).$$

*Income from Property.*

(a) When  $x \leq 350$ ,

$$T = 0.$$

(b) When  $350 < x \leq 500$ ,

$$\begin{aligned} T &= (x - 350) \left[ 7 \cdot 75 + (x - 350) \frac{5}{1000} \right] \\ &= \frac{5}{1000}x^2 + 4 \cdot 25x - 2100. \end{aligned}$$

(c) When  $500 < x \leq 1000$ ,

$$\begin{aligned} T &= 2 \cdot 55 \times 500 + (x - 500) \left[ 28 + \frac{3}{100}(x - 500) \right] \\ &= \frac{3}{100}x^2 - 2x - 5225. \end{aligned}$$

(d) When  $1000 < x \leq 2000$ ,

$$\begin{aligned} T &= 22 \cdot 775 \times 1000 + (x - 1000) \left[ 58 + \frac{22}{1000}(x - 1000) \right] \\ &= \frac{22}{1000}x^2 + 14x - 13,225. \end{aligned}$$

(e) When  $2000 < x \leq 5000$ ,

$$\begin{aligned} T &= 51 \cdot 3875 \times 2000 + (x - 2000) \left[ 102 + \frac{8}{1000}(x - 2000) \right] \\ &= \frac{8}{1000}x^2 + 70x - 69,225. \end{aligned}$$

(f) When  $5000 < x \leq 10,000$ ,

$$\begin{aligned} T &= 96 \cdot 155 \times 5000 + (x - 5000) \left[ 150 + \frac{12}{10000}(x - 5000) \right] \\ &= \frac{12}{10000}x^2 + 138x - 239,225. \end{aligned}$$

(g) When  $x > 10,000$ ,

$$T = 126 \cdot 0775 \times 10,000 + 162(x - 10,000).$$

IV.

It will be noticed that all the amounts in Section III (except for  $x > 10,000$ ) are expressed in the form  $ax^2 + bx + c$ . The total amount payable (Income Tax plus Social Services Contribution) is also expressible in this form. Following

Carslaw's notation, if  $T(x)$  denote the amount payable on an income of  $\pounds x$ , the  $x$ th  $\pounds$  pays an amount  $T(x) - T(x-1)$ , an expression of the form  $a(2x-1)+b$ . It is this increment which interests the taxpayer concerned about the amount of tax payable on additional income.

*Earned Income.*

There is no income tax on incomes not exceeding  $\pounds 500$ ; the amount of contribution payable is

$$x \left[ 3 + \frac{3}{80}(x-100) \right] \\ = \frac{3}{80}x^2 - \frac{3}{4}x.$$

The  $x$ th  $\pounds$  therefore pays  $\frac{3}{80}(2x-1) - \frac{3}{4}$  pence. For example, at  $x=400$  the amount of contribution is 5700 pence; the rate  $\left(\frac{T}{x}\right)$  is 14.25 pence per  $\pounds$ . The 401st  $\pounds$  pays 29.2875 pence.

When  $x$  exceeds 500, the Social Services Contribution remains 18 pence per  $\pounds$ . The total amount payable on an income of  $\pounds x$  is thus

$$ax^2 + bx + c + 18x$$

the values of  $a$ ,  $b$ ,  $c$  being those given in Section II for the various income ranges. The amount payable on the  $x$ th  $\pounds$  is  $[a(2x-1)+b+18]$  pence. For any given range, these increments form an arithmetic progression with common difference  $2a$ .

Thus, the 501st  $\pounds$  pays 36.024 pence; the common difference for the range is 0.048 and the 1000th  $\pounds$  pays 59.976 pence.

The 1001st  $\pounds$  pays 60.02 pence; the common difference is 0.040 and the 2000th  $\pounds$  pays 99.98 pence.

The 2001st  $\pounds$  pays 100.01 pence; the common difference is 0.020 and the 5000th  $\pounds$  pays 159.99 pence.

The 5001st  $\pounds$  pays 160.002 pence; the common difference is 0.004 and the 10,000th  $\pounds$  pays 179.999 pence.

The 10,001st  $\pounds$  pays 180 pence. This is the maximum rate.

It is interesting to note that the 3001st  $\pounds$  pays 120.02 pence. For a taxpayer without dependents it is only on income in excess of  $\pounds 3000$  that more than half of every additional pound is paid out in tax.

*Income from Property.*

For property incomes, tax begins at  $\pounds 350$ , before the Social Services Contribution has reached the maximum rate. From the expressions for Tax and Contribution, the following formula for the total amount payable is obtained

$$\frac{42.5}{1000}x^2 + 3.5x - 21,000 \quad 350 < x \leq 500.$$

The 351st  $\pounds$  pays 33.2925 pence; the common difference is 0.085 and the 500th  $\pounds$  pays 45.9575 pence.

For incomes in excess of  $\pounds 500$  the calculation of the increment is carried out in the same way as for earned income, the values of  $a$  and  $b$  corresponding

to a given value of  $x$  being ascertained from the formulæ of Section III. For example, if  $1000 < x \leq 2000$ ,  $a=0.022$ ,  $b=14$ . The 1001st £ pays a total of  $58.022 + 18 = 76.022$  pence; this increment increases by 0.044 pence per £ and the 2000th £ pays 119.978 pence. For property incomes the increment exceeds 10/- in the £ when  $x$  exceeds 2000. The maximum rate of 180 pence is again reached at incomes of £10,000, but the approach to this rate is more rapid than for earned income.

## V.

Figure 1 shows the total amount (Tax and Contribution) by each £ of income received in the year ending June 30th, 1950, for a taxpayer entitled to no rebates. The procedure followed is that given by Carslaw.

If the total amount payable has the form  $ax^2 + bx + c$ , the amount paid by the  $x$ th £ has been shown to be  $[a(2x-1) + b]$  pence. Thus the line  $y = 2ax + b$  has for the ordinate at  $x - \frac{1}{2}$  the amount of tax on the  $x$ th £. For earned income

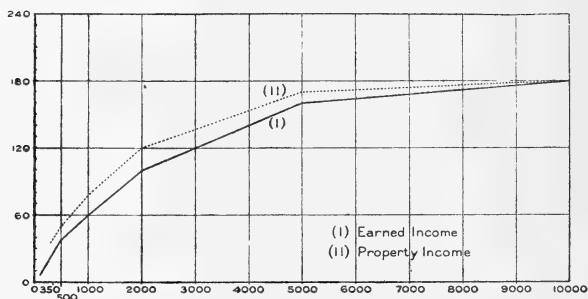


Fig. 1.

the graph will be made up of line segments corresponding to the ranges (a) to (f) of Section III. We shall assume  $x > 105$ . The equations of the lines are given below.

$$(a) \quad x \leq 500$$

$$y = \frac{3}{40}x - \frac{3}{4}$$

$$(b) \quad 500 < x \leq 1000$$

$$y = \frac{48}{1000}x + 12$$

$$(c) \quad 1000 < x \leq 2000$$

$$y = \frac{40}{1000}x + 20$$

$$(d) \quad 2000 < x \leq 5000$$

$$y = \frac{20}{1000}x + 60$$

$$(e) \quad 5000 < x \leq 10,000$$

$$y = \frac{4}{1000}x + 140.$$

When  $x > 10,000$  the constant maximum rate is given by  $y = 180$ .

Similarly, the lines making up the graph relevant to Property Income are:

$$(a) \quad x \leq 350$$

$$y = \frac{75}{1000}x - \frac{3}{4}$$

$$(b) \quad 350 < x \leq 500$$

$$y = \frac{85}{1000}x + 3.5$$

$$(c) \quad 500 < x \leq 1000$$

$$y = \frac{60}{1000}x + 16$$

$$\begin{aligned}
 (d) \quad 1000 < x \leq 2000 & \quad y = \frac{44}{1000}x + 32 \\
 (e) \quad 2000 < x \leq 5000 & \quad y = \frac{16}{1000}x + 88 \\
 (f) \quad 5000 < x \leq 10,000 & \quad y = \frac{2.4}{1000}x + 156 \\
 (g) \quad x > 10,000 & \quad y = 180.
 \end{aligned}$$

It will be observed that there is an irregularity in the graph describing the amount payable on property income. This results from the commencement of Income Tax at  $x=350$ , before the Contribution rate has reached its maximum value.

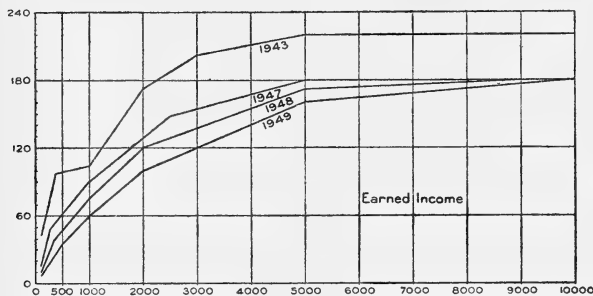


Fig. 2.

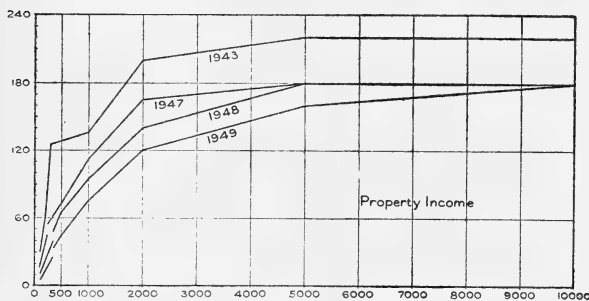


Fig. 3.

Figures 2 (Earned Income) and 3 (Property Income) compare the rates prevailing in 1943 (the year of maximum taxation), 1947, 1948 and 1949. Figure 2 shows that for incomes up to £1000 per annum it is no longer true that incentive to increase output is destroyed by the excessive taxation on additional earnings (overtime, etc.), the additional tax, even for a taxpayer without dependents, being always less than five shillings in the £.

#### REFERENCE

Carslaw, H. S., 1947. The Australian Social Services Contribution and Income Tax Acts, 1947. *The Economic Record*, pp. 3-11. References to papers on the earlier Acts are given in this paper.

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## STUDIES IN THE CHEMISTRY OF PLATINUM COMPLEXES.

### PART I. TETRAMMINE PLATINUM (II) FLUORIDES.

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A survey of the literature on platinum and fluorine indicates very little is known on the chemistry of platinum fluorides. Platinum (II) and platinum (IV) fluorides have been reported (Mellor, 1937). Fluoroplatinates (IV) of sodium, potassium and ammonium have also been prepared (Mellor, 1937),  $K_2PtF_6$  (Schlesinger and Tapley, 1924) being a pale yellow crystalline compound sparingly soluble in water, in which it is relatively stable. Among the platinum complexes, Hedin (1886) reported the possible existence of difluoro dipyridine platinum (II).  $[Pt(NH_2OH)_4](HF_2)_2 \cdot 2H_2O$  has also been prepared (Goremykin, 1944).

In this investigation the fluorides and hydrogen fluorides of the complex ion  $[PtA_4]^{++}$  have been prepared ( $A = NH_3$ ,  $C_5H_5N$ ;  $2A = C_2H_4(NH_2)_2$ ). These are all colourless substances, crystallising in well-formed crystals from water or aqueous acetone, often with water of crystallisation, part of which is lost on drying over  $P_2O_5$ . They were all readily soluble in water, the solution of the hydrogen fluorides having a distinctly acid reaction and liberating  $CO_2$  from carbonates. The ion  $[PtA_4]^{++}$  was quite stable in the presence of excess hydrofluoric acid, and the salts could be evaporated with 46% acid at the boiling point without decomposition.

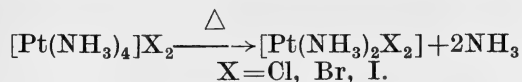
Hydrogen fluorides prepared by evaporation to dryness in this fashion yielded salts of the type  $[Pt(NH_3)_4](HF_2)_2$ . These salts were stable in a dry atmosphere but exposure to air resulted in the loss of HF, glass in the immediate vicinity being etched. The effect was greatest with the ethylenediamino and least with the pyridino compounds. Further, when  $[Pt\{C_2H_4(NH_2)_2\}_2](HF_2)_2$  was dissolved in aqueous hydrofluoric acid solution and crystallised by the addition of acetone, the compound  $[Pt\{C_2H_4(NH_2)_2\}_2]HF_2 \cdot F \cdot H_2O$  was obtained, in which one  $HF_2^-$  anion had been replaced by a  $F^- \cdot H_2O$  group. The same tendency was probably operative in the case of the  $[Pt(NH_3)_4](HF_2)_2$  salt. Whenever crystallised from aqueous acid solution by the addition of acetone, the compound contained less F than required by formula. It is possible that a continuous series of compounds, containing mixed anions, exist intermediate between  $[Pt\{C_2H_4(NH_2)_2\}_2](HF_2)_2$  and  $[Pt\{C_2H_4(NH_2)_2\}_2]^{F \cdot H_2O}_{HF_2^-}$ , in which the  $H_2O$  is strongly held by the hydrogen bonds to the  $F^-$  anion, so that the  $HF_2^-$  can be replaced by  $F^- \cdot \dots H-O-H$  without alteration to the structure.

The stability of the complex ion towards hydrofluoric acid contrasts strongly with its behaviour towards other halogen acids. Thus it is well known that the addition of hydrochloric acid to  $[Pt(NH_3)_4]Cl_2$  results in the formation of  $[Pt(NH_3)_2Cl_2]$ . That this difference cannot be attributed wholly to the fact that hydrofluoric acid is a comparatively weak acid is supported by the fact that  $[Pt(NH_3)_4]I_2$  passes readily to  $[Pt(NH_3)_2I_2]$  on boiling the aqueous solution.



Thus it must be assumed that the lack of reaction between  $[\text{Pt}(\text{NH}_3)_4]^{++}$  and HF is due in some measure to the reluctance of Pt and F to form a covalent bond.

The stability of these compounds to heat is in process of investigation in order to compare with the general reaction of the type



Preliminary experiments on the behaviour of the cis and trans diammine bases,  $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]$  etc., with hydrofluoric acid have indicated anomalous results. The results of these experiments will be reported in later papers in this series.

#### EXPERIMENTAL.

(All operations involving fluorides were carried out in platinum or paraffin vessels. The hydrofluoric acid used was A.R. quality (General Chemical Co., U.S.A.) with analysis 0.15%  $\text{H}_2\text{SiF}_6$  (max.).

##### *Tetrammine Platinum (II) Hydrogen Fluoride.*

$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$  was prepared ("Inorganic Syntheses", II, 250).

Found: Pt, 55.6%; Cl, 20.3%. Calculated: Pt, 55.4%; Cl, 20.1%.

$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (0.5 g.) was converted to a solution of  $[\text{Pt}(\text{NH}_3)_2](\text{OH})_2$  with  $\text{Ag}_2\text{O}$ . After separation of  $\text{AgCl}$  and excess  $\text{Ag}_2\text{O}$ , the solution was acidified with excess HF, evaporated to near dryness on the water bath and finally dried in an air oven at about 70° C. until excess HF expelled. The residue was further dried *in vacuo* over  $\text{CaCl}_2$  for several days. Under microscope, the compound consisted of clear, colourless quadrilateral plates with angles  $\neq 90^\circ$ . The compound was readily soluble in water, the solution having a distinctly acid reaction. Yield, 0.4 g. On exposure to air the compound lost HF, glass in the vicinity being etched.

Found: Pt, 56.9%; F, 21.7%.

$[\text{Pt}(\text{NH}_3)_4](\text{HF})_2$  requires Pt, 57.2%; F, 22.3%.

The method was varied by crystallising the salt from aqueous hydrofluoric solution with acetone. The compound crystallised in long thin needles.

Found (dried over  $\text{P}_2\text{O}_5$ ): Pt, 57.1%; F, 20.3%.

Recrystallised aqueous HF + acetone, Pt, 57.3%; F, 20.5%.

##### *Tetrammine Platinum (II) Fluoride 1.5 Hydrate.*

$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , 5.0 g., was converted to a solution of the corresponding hydroxide as before and the solution divided into two equal portions. One portion was converted to the solid hydrogen fluoride and the second portion then added. After evaporation the compound was crystallised by the addition of acetone. Recrystallised from aqueous acetone. Yield, 4.1 g.  $[\text{Pt}(\text{NH}_3)_4]\text{F}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  was readily soluble in water, the solution having an alkaline reaction (litmus). From aqueous acetone the compound was obtained in very fine white microcrystals. On heating at 100° C. only  $1\text{H}_2\text{O}$  is lost, the remaining  $\frac{1}{2}\text{H}_2\text{O}$  being held strongly in the compound, probably by hydrogen bonds to the fluoride ion.

Found (on air-dry material): Pt, 59.9%; F, 11.1%;  $\text{H}_2\text{O}$ , 5.8% (loss in one hour at 100° C.).

$\text{Pt}(\text{NH}_3)_4\text{F}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  requires Pt, 59.5%; F, 11.6%. Loss for  $1\text{H}_2\text{O}$ , 5.5%.

##### *Tetrapyridine Platinum (II) Hydrogen Fluoride 6-Hydrate.*

$[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  (Drew, Pinkard, Wardlaw and Cox, 1932) was recrystallised from aqueous acetone.

Found: Pt, 30.7%; Cl, 11.1%. Calculated: Pt, 30.7%; Cl, 11.1%.

3.0 g. were treated in the same manner as described for the corresponding tetrammino compound. From aqueous HF solution  $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4](\text{HF}_2)_2 \cdot 6\text{H}_2\text{O}$  crystallised in white opaque rectangular plates on the addition of acetone; yield, 1.0 g. The compound was very soluble in water, the solution having a distinctly acid reaction. Over  $\text{P}_2\text{O}_5$ ,  $5\frac{1}{2}\text{H}_2\text{O}$  are lost, the remaining  $\frac{1}{2}\text{H}_2\text{O}$  being lost on heating to  $100^\circ\text{C}$ . The dehydrated salt very slowly absorbs  $\text{H}_2\text{O}$  from the air. On exposure to air the salt slowly loses HF, this effect being less than with the corresponding tetrammino salt.

Found (on air-dry material): Pt, 28.0%; F, 10.7%;  $\text{H}_2\text{O}$ , 14.1%, 14.2% (loss *in vacuo* over  $\text{P}_2\text{O}_5$ ), 15.4% (loss in one hour at  $100^\circ$ ).

$[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4](\text{HF}_2)_2 \cdot 6\text{H}_2\text{O}$  requires Pt, 28.0%; F, 10.9%. Loss for  $5\frac{1}{2}\text{H}_2\text{O}$ , 14.2%; loss for  $6\text{H}_2\text{O}$ , 15.5%.

*Tetrapyridine Platinum (II) Fluoride 9-Hydrate.*

5.0 g. of the corresponding chloride were treated by the method employed for the corresponding tetrammino compound. From the aqueous solution  $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]\text{F}_2 \cdot 9\text{H}_2\text{O}$  crystallised in clear colourless cubes and octahedra on the addition of acetone. Recrystallised from aqueous acetone. Yield, 3.3 g. The compound was readily soluble in water, giving a distinctly alkaline reaction with litmus paper. The salt readily loses  $6\text{H}_2\text{O}$  on drying over  $\text{P}_2\text{O}_5$ . The trihydrate is stable to  $100^\circ$ , at which temperature decomposition is commencing, pyridine being lost and the residue turning yellow. The trihydrate rapidly takes up six moles of  $\text{H}_2\text{O}$  on exposure to air.

Found (air-dry material): Pt, 27.6%; F, 5.3%;  $\text{H}_2\text{O}$ , 15.1%, 15.7% (loss *in vacuo* over  $\text{P}_2\text{O}_5$ ).

$[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]\text{F}_2 \cdot 9\text{H}_2\text{O}$  requires Pt, 27.4%; F, 5.3%. Loss for  $6\text{H}_2\text{O}$ , 15.2%.

*Bis(ethylenediamine) Platinum (II) Hydrogen Fluoride.*

Bis(ethylenediamine) platinum (II) chloride was prepared by the action of aqueous ethylenediamine on  $\text{K}_2\text{PtCl}_4$ , filtering the insoluble  $[\text{Pt}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2]\text{Cl}_2$  and dissolving in aqueous ethylenediamine.  $[\text{Pt}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2]\text{Cl}_2$  crystallised on the addition of alcohol-acetone. Recrystallised from hot water.

Found: Pt, 50.5%; Cl, 18.3%. Calculated: Pt, 50.5%; Cl, 18.4%.

1.0 g. was converted at the corresponding hydroxide and the solution evaporated with excess HF in the same manner as described for the corresponding tetrammino compound. After evaporation on the water bath the residue was baked in an air oven at  $110^\circ\text{C}$ . Yield, 1.1 g. Examined under microscope, the material consisted of broken, jagged, colourless crystals. The compound was slightly deliquescent and readily soluble in water, the solution having a distinctly acid reaction. On exposure to air HF is readily lost, glass in the vicinity being badly etched.

Found (material dried over  $\text{CaCl}_2$ ): Pt, 49.5%; F, 18.9%.

$[\text{Pt}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2](\text{HF}_2)_2$  requires Pt, 49.6%; F, 19.3%.

*Bis(ethylenediamine) Platinum II Fluoride Hydrogen Fluoride 1-Hydrate.*

A solution of the hydrogen fluoride, prepared as above, in aqueous hydrofluoric acid, was crystallised by the addition of acetone. The compound crystallised in clear colourless rectangular plates. The dry compound gave an acid reaction with moist litmus paper.

Found (material dried over  $\text{P}_2\text{O}_5$ ): Pt, 49.8%; F, 13.8%.

$[\text{Pt}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2]_{\text{HF}_2}^{\text{F} \cdot \text{H}_2\text{O}}$  requires Pt, 49.9%; F, 14.5%.

*Bis(ethylenediamine) Platinum (II) Fluoride 2-Hydrate.*

5.0 g. of the chloride treated as described for the corresponding tetrammine compound. After concentration the compound was crystallised by the addition of acetone. Yield, 4.4 g. Recrystallised from aqueous acetone. Yield, 4.1 g. The compound which crystallised in clear

colourless quadrilateral plates with angles  $\neq 90^\circ$ , was readily soluble in water to give an alkaline solution (litmus). Over  $P_2O_5$ ,  $1\frac{1}{2}H_2O$  are lost, the remaining  $\frac{1}{2}H_2O$  being very strongly held.

Found (air-dry material): Pt, 49.6%; F, 9.5%;  $H_2O$ , 7.2%, 6.6% (loss over  $P_2O_5$  no further loss on heating two hours at  $140^\circ C$ ).

$[Pt\{C_2H_4(NH_2)_2\}_2]F_2 \cdot 2H_2O$  requires Pt, 50.1%; F, 9.8%;  $2H_2O$ , 9.3%;  $1\frac{1}{2}H_2O$ , 7.0%.

#### Analyses.

Platinum analyses were made by igniting 0.1 g. of material in a platinum crucible. Fluorine was determined by boiling 0.1 g. material with excess aqueous ammonia until the odour of ammonia was faint and then by the standard method of adding sodium carbonate and precipitating calcium carbonate and fluoride with calcium chloride. The separated material was ignited in a platinum crucible treated with excess acetic acid and evaporated to dryness on the water bath. The calcium fluoride was filtered, ignited and weighed. The calcium fluoride was converted to calcium sulphate as a check. Finally the calcium sulphate was dissolved in diluted hydrochloric acid and a small quantity of platinum (usually  $<0.5$  mg.) was filtered, ignited and weight deduced from calcium fluoride and calcium sulphate. Good agreement between calcium sulphate and calcium fluoride weight was obtained in each case. The fluoride percentage was not corrected for small solubility of calcium fluoride in the water used for washing the precipitate. It is estimated that in compounds with 20% and 10% F. the result would probably be low by 2% and 4% respectively.

#### SUMMARY.

The preparation of the fluorides and hydrogen fluorides of  $[Pt(NH_3)_4]^{++}$ ,  $[Pt(C_5H_5N)_4]^{++}$ , and  $[Pt\{C_2H_4(NH_2)_2\}_2]$  are described. They are all well defined, colourless crystalline compounds, readily soluble in water. Evidence was obtained that compounds with mixed fluoride and hydrogen fluoride anions exist.

#### ACKNOWLEDGEMENTS.

The author is indebted to Dr. P. F. J. Dwyer for initially suggesting this programme and for his interest and suggestions during the course of the work.

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PART IV

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# INVOLUTIONS ON A CONIC AND ORTHOGONAL MATRICES.

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(Communicated by PROFESSOR T. G. ROOM, F.R.S.)

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Let  $s$  be a given non-degenerate conic in a plane  $\pi$ . Each point  $P$  of  $\pi$  ( $P$  not on  $s$ ) determines an involutory self-transformation  $P$  of  $s$  and every such transformation is determined by a point of  $\pi$  not on  $s$ . (The identity will not be regarded as an involution here.) If a line through  $P$  meets  $s$  in points  $U, V$  we shall write  $UP=V$ . If  $Q$  is any point of  $\pi$  and  $VQ$  meets  $s$  again in  $W$ , we write

$$UPQ=VQ=W.$$

It is clear that the operators  $P, Q, \dots$  form a multiplicative set which are fully associative; the product of any number of these operators is a projectivity which is not, in general, an involution. The involutory transformations of a conic form a subset, never a subgroup, of the group of transformations of the conic.

The aim of the first part of this paper is to discuss the conditions under which the product  $A_1A_2 \dots A_{n-1}$  of a number of involutions is an involution  $A_n$ . This is equivalent to the conditions that

$$A_1A_2 \dots A_n = I \tag{1}$$

where  $I$  is the identical transformation.

The problem of inscribing a polygon  $P_1P_2 \dots P_n$  in  $s$  so that  $P_iP_{i+1}$  passes through  $A_i$  ( $A_1, \dots, A_n$  being  $n$  given distinct points) is known to have two solutions in general. [See, e.g., Salmon, 1850.] The condition that this problem have an infinity of solutions is obviously that the relation (1) above should hold.

For the case  $n=2$  we see at once that  $A_1A_2=I$  if, and only if,  $A_1=A_2$ , i.e.  $A_1=A_2$ .

For  $n=3$  we shall prove

*Theorem 1.* A necessary and sufficient condition that  $A_1A_2A_3=I$  is that  $A_1A_2A_3$  should be a self-polar triangle with respect to  $s$ .

Given that  $A_1A_2A_3=I$ , let  $A_1A_2$  meet  $s$  in points  $U, V$ . So  $UA_1A_2A_3=U$  and  $UA_1A_2=U$ ; therefore  $UA_3=U$ . I.e.  $A_3$  lies on the tangent at  $U$ .

Similarly, we see that  $A_3$  must lie on the tangent at  $V$ ; and therefore  $A_3$  is the pole of  $A_1A_2$ .

Since  $A_1A_2A_3=I$  and  $A_3^2=I$  we have

$$A_3A_1A_2=I.$$

Therefore  $A_2$  is the pole of  $A_3A_1$ . Hence  $A_1A_2A_3$  is a self-polar triangle.

The above proof breaks down if  $U$  and  $V$  coincide. In this case  $A_1, A_2, A_3$  would have to be collinear on a tangent of  $s$ . It will be seen from Theorem 2 below that, if  $A_1, A_2, A_3$  are collinear then  $A_1A_2A_3$  is always an involution and therefore cannot be the identity. Thus  $U$  and  $V$  would never coincide.

Conversely, if  $A_1A_2A_3$  is a self-polar triangle, take any point  $P$  on  $s$  and let  $PA_1=Q$ ,  $QA_2=R$ ,  $RA_1=S$ ,  $SA_2=P'$ . If  $A_2A_3$  meets  $A_1P$  and  $A_1S$  in  $A_1'$  and  $A_1''$  respectively, then

$$(A_1A_1', PQ) = -1 = (A_1A_1'', RS).$$

Hence  $P$  and  $P'$  coincide and  $PR$ ,  $QS$  must meet at  $A_3$ . Therefore  $RA_3=P$  and so

$$PA_1A_2A_3=P \text{ or } A_1A_2A_3=I.$$

*Corollary 1.* The necessary and sufficient condition that  $AB$  be an involution is that  $A$ ,  $B$  be conjugate points with regard to  $s$ .

*Corollary 2.* If the product of  $A$ ,  $B$  and  $C$  in any one order is the identity then it is so for every order. (This is also obvious algebraically.)

For the case  $n=4$  we shall prove :

*Theorem 2.* A necessary and sufficient condition that  $A_1A_2A_3A_4=I$  is that  $A_1, \dots, A_4$  be collinear on a line  $l$  meeting  $s$  in  $U$ ,  $V$  such that  $(U, V)$ ,  $(A_1, A_3)$ ,  $(A_2, A_4)$  are pairs of an involution on  $l$ .

First, notice that if  $PAB=P$  then  $A$ ,  $B$ ,  $P$  are collinear.

Given that  $A_1 \dots A_4=I$ , let  $A_1A_2$  meet  $s$  in  $U$ ,  $V$ . Then  $UA_1A_2=U$  and  $VA_1A_2=V$ .

But  $A_1A_2=A_4A_3$ ; therefore  $UA_4A_3=U$  and  $VA_4A_3=V$ . So  $A_3$  and  $A_4$  must lie on  $UV$ ; i.e.,  $A_1, \dots, A_4$  are collinear. (The proof is still valid if  $U$  and  $V$  coincide.)

Now take any point  $P$  on  $s$  and let  $PA_1=Q$ ,  $QA_2=R$ ,  $RA_3=S$ . Therefore  $SA_4=P$ . Hence  $(U, V)$ ,  $(A_1, A_3)$ ,  $(A_2, A_4)$  are pairs of an involution.

The converse result is easily proved.

*Corollary.* The product of three involutions  $ABC$  is an involution if, and only if,  $A$ ,  $B$ ,  $C$  are collinear.

Before treating the general value of  $n$  we shall require the following

*Lemma A.* Any projective transformation  $L$  of  $s$  into itself can be expressed as the product of two involutions and this can be done in  $\infty^1$  ways.

For, let  $U$ ,  $V$  be the self-corresponding points of the projectivity  $L$  and let  $PL=Q$  where  $P$  is an arbitrarily chosen point of  $s$ . Take any point  $M$  on  $UV$  and let  $PM$  meet  $s$  again in  $R$  and  $RQ$  meet  $UV$  in  $N$ .

Now  $PLNM=P$ , and also

$$ULNM=U, VLNLM=V.$$

Thus  $U$ ,  $V$ ,  $P$  are three distinct self-corresponding points of the projectivity  $LNM$  which must therefore be the identity.

Hence  $L=MN$ .

$M$  was chosen arbitrarily on  $UV$  and  $N$  was then uniquely determined; thus  $L$  is expressible as the product of two involutions in  $\infty^1$  ways.

If the given projectivity is parabolic the theorem is still true but the above proof will need modification.

We now discuss our initial problem for a general value of  $n(>4)$ .

$A_1A_2 \dots A_{n-2}$ , being a projectivity, is, by the above lemma, expressible as the product of two involutions  $MN$ . Moreover, if  $U$ ,  $V$  are the self-corresponding points of this projectivity, then  $M$ ,  $N$  lie on  $UV$ .

The condition that

$$A_1 A_2 \dots A_n = I$$

will therefore be the condition that

$$MNA_{n-1}A_n = I.$$

From Theorem 2 it follows that this is equivalent to the condition that  $A_{n-1}$  and  $A_n$  should lie in  $UV$  and that  $(U, V), (M, A_{n-1}), (N, A_n)$  be pairs of points in involution.

Since  $A_1 \dots A_{n-2} \neq I$  (we assume that  $A_1 \dots A_n$  contains no superfluous factors) it follows that there exist just two polygons of  $(n-2)$  sides inscribed in  $s$  with their sides passing through  $A_1, \dots, A_{n-2}$  in order,  $U$  being the first vertex of one polygon and  $V$  the first vertex of the other.

We have thus proved

*Theorem 3.* A necessary and sufficient condition that  $ABC \dots PQ$  be an involution is that the point  $Q$  should lie on the line joining the self-corresponding points of the projectivity  $ABC \dots P$ .

The following deductions are immediate.

*Corollary 1.* The freedom of sets of points  $A_1, \dots, A_n$  such that  $A_1 A_2 \dots A_n = I$  is  $2n-3$ .

*Corollary 2.* If  $A_1 A_2 \dots A_n = I$  then the self-corresponding points of the transformation  $A_{i+2} A_{i+3} \dots A_n A_1 \dots A_{i-1}$  are the intersections of  $A_i A_{i+1}$  with  $s$ .

*Corollary 3.* If  $A, B, \dots, J, K$  be an odd number of points lying on a line  $l$  then  $AB \dots K$  is an involution. (The self-corresponding points of  $AB \dots J$  are the intersections of  $l$  with  $s$ .)

#### *Algebraic Contents of the Results.*

Taking the conic  $s$  in the form

$$x_0 : x_1 : x_2 = t_1^2 : t_0 t_1 : t_0^2$$

where  $(x_0, x_1, x_2)$  are homogeneous coordinates in the plane and  $(t_0, t_1)$  homogeneous parameters, the involutory self-transformation  $P$  of  $s$  determined by the point  $P(p_0, p_1, p_2)$  may be expressed thus :

$$\begin{pmatrix} t_0 \\ t_1 \end{pmatrix} = \begin{pmatrix} p_1 & -p_0 \\ p_2 & -p_1 \end{pmatrix} \begin{pmatrix} t_0^* \\ t_1^* \end{pmatrix}$$

where  $p_0 p_2 - p_1^2 \neq 0$  since  $P$  does not lie on  $s$ . Writing

$$P = \begin{pmatrix} p_1 & -p_0 \\ p_2 & -p_1 \end{pmatrix} \quad (2)$$

we see that  $P$  is fully characterised by the (non-singular) matrix  $P$  which is called an involutory matrix. [ $P^2 = (p_0 p_2 - p_1^2)I$ .] In other words, a 2 by 2 matrix is involutory if, and only if, it is of the form (2).

The above theorems, obtained geometrically, yield at once the following algebraic results.

*Theorem 4.* The product of two involutory 2 by 2 matrices  $AB$  is an involutory matrix, if, and only if,

$$a_0 b_2 + a_2 b_0 - 2a_1 b_1 = 0,$$

where

$$A = \begin{pmatrix} a_1 & -a_0 \\ a_2 & -a_1 \end{pmatrix} \text{ etc.}$$

**Theorem 5.** The product of three 2 by 2 involutory matrices  $\mathbf{ABC}$  is an involutory matrix if, and only if,

$$\begin{vmatrix} a_0 & a_1 & a_2 \\ b_0 & b_1 & b_2 \\ c_0 & c_1 & c_2 \end{vmatrix} = 0.$$

**Theorem 6.** Let  $\mathbf{A}, \mathbf{B}, \dots, \mathbf{J}, \mathbf{K}$  be a set of involutory 2 by 2 matrices and let  $\mathbf{AB} \dots \mathbf{J} = \mathbf{R}$  where  $\mathbf{R}$  may, or may not, be involutory. If the eigen-vectors of  $\mathbf{R}$  be  $(r_{01}, r_{11})$  and  $(r_{02}, r_{12})$  then a necessary and sufficient condition that  $\mathbf{AB} \dots \mathbf{JK}$  be an involutory matrix is

$$\begin{vmatrix} r_{01}^2 & r_{01}r_{11} & r_{11}^2 \\ r_{02}^2 & r_{02}r_{12} & r_{12}^2 \\ k_0 & k_1 & k_2 \end{vmatrix} = 0,$$

where

$$\mathbf{K} = \begin{pmatrix} k_1 & -k_0 \\ k_2 & -k_1 \end{pmatrix}$$

[An eigen-vector of an  $n$  by  $n$  matrix  $\mathbf{A}$  is a non-zero vector  $\mathbf{x}$  satisfying  $\mathbf{Ax} = \lambda\mathbf{x}$  for an appropriate scalar  $\lambda$ . There are, in general,  $n$  independent eigen-vectors corresponding to the  $n$  values of  $\lambda$  given by  $|\lambda\mathbf{I} - \mathbf{A}| = 0$ .]

Theorem 3, Corollary 3, gives

**Theorem 7.** If  $\mathbf{A}_1, \dots, \mathbf{A}_n$  be an odd number of involutory 2 by 2 matrices, where

$$\mathbf{A}_i = \begin{pmatrix} a_{1i} & -a_{0i} \\ a_{2i} & -a_{1i} \end{pmatrix},$$

then the relations

$$\begin{vmatrix} a_{01} & a_{02} & \dots & a_{0n} \\ a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \end{vmatrix} = 0$$

imply that the product  $\mathbf{A}_1\mathbf{A}_2 \dots \mathbf{A}_n$  is an involutory matrix.

**Corollary.** If  $\mathbf{A}$  and  $\mathbf{B}$  are involutory then so are  $(\mathbf{AB})^n\mathbf{A}$  and  $(\mathbf{AB})^n\mathbf{B}$ . This is also obvious algebraically and holds for square matrices of any order.

### Relation to Orthogonal Matrices.

We now consider the relation of the above results to orthogonal matrices of order three. In the remainder of this paper all matrices denoted by capital letters are square matrices of the third order, all vectors are denoted by lower case letters and are regarded as 3 by 1 matrices, and the transpose of a matrix will be signified by a dash. For any vector such as  $\mathbf{a}$  we shall assume that  $\mathbf{a}' = (a_1, a_2, a_3)$ . Also, a point  $P$  of coordinates  $(p_1, p_2, p_3)$  shall be referred to as the point  $\mathbf{p}$  or the point of coordinate vector  $\mathbf{p}$  (i.e. using the corresponding lower case symbol).

If the conic  $s$ , used above, be taken in the plane  $\pi$  at infinity ( $x_0 = 0$ ) with equation

$$x_1^2 + x_2^2 + x_3^2 = 0,$$

then any (non-singular) collineation of the plane  $\pi$  into itself which leaves  $s$  invariant is an orthogonal transformation; and the converse is true. Writing this collineation as

$$\rho\mathbf{x}^* = \mathbf{Ax}$$

then  $\mathbf{A}$  may be taken as an orthogonal matrix. If  $\mathbf{A}$  is real with determinant equal to  $+1$  then this transformation corresponds to a proper rotation in ordinary cartesian space.

In the geometrical results above we were concerned exclusively with transformations of the points on the conic  $s$ . It is clear that any projectivity on  $s$  can be extended into a collineation of the whole plane  $\pi$  and, moreover, this extension is unique. For, if  $T$  and  $T^*$  are two such extensions then  $T^{-1}T^*$  would leave every point of the non-degenerate conic  $s$  invariant. On examining the possible types of collineations in a plane corresponding to the six distinct Segre characteristics, [Todd, 1947] it follows that  $T^{-1}T^*$  must be the identity; that is,  $T=T^*$ .

In particular the involution  $P$  on  $s$  corresponding to the point  $P$  extends (uniquely) into an involutory collineation of  $\pi$ , namely, the harmonic inversion in the point  $P$  and its polar  $p$  with respect to  $s$ . We shall refer to this as the involutory collineation  $P$  determined by the point  $P$ . This can be interpreted in ordinary cartesian space as a reflection of (unsensed) lines through the origin  $O$  in a plane through  $O$ .

The matrix of the involutory collineation  $P$  is easily found as follows. The polar of the point  $P$ , of coordinate vector  $p$ , with respect to the conic  $x'Ax$ , is  $p'Ax=0$ . Denoting the involutory collineation determined by  $P$  by

$$\kappa x^* = Px,$$

we see that  $x$  and  $x^*$  must be of the form

$$x = \lambda p + q \quad \text{and} \quad x^* = -\lambda p + q$$

where  $q$  is the point of intersection of the polar of  $P$  with the line joining  $P$  to  $x$ . Therefore

$$x^* = x - 2\lambda p.$$

Since  $Q$  lies on the polar of  $P$

$$p'A(x - \lambda p) = 0,$$

giving

$$\lambda = (p'Ax) / p'Ap.$$

Hence

$$\kappa x^* = \left( I - \frac{2pp'A}{p'Ap} \right) x,$$

and so  $P$  may be taken in the form

$$P = \rho \left( I - \frac{2pp'A}{p'Ap} \right).$$

Now the coordinate vectors of points not on  $s$  may be normalised to unit magnitude and the conic  $s$  may be taken as  $x'x=0$ . Then  $A=I$ ,  $p'p=1$  and we have  $P$  in the form (taking  $\rho=-1$  to make  $|P|=1$ ),

$$P = -I + 2pp'. \quad (3)$$

$P$  is symmetric, orthogonal and involutory (any two of these adjectives imply the third). Moreover, it is clear that every symmetric proper orthogonal matrix of the third order must be expressible in the form (3).

Theorem 1, Corollary 1, therefore yields

*Theorem 8.* The product of two symmetric orthogonal matrices  $P$ ,  $Q$  is also symmetric and orthogonal if, and only if,  $p'q=0$ .

Interpreted in ordinary cartesian space this may be stated as follows:

The product of two reflections, in planes  $\alpha$ ,  $\beta$ , is a reflection if, and only if,  $\alpha$  is perpendicular to  $\beta$ . (The reflections are of unsensed lines through the origin  $O$  in planes through  $O$ .)

Theorem 2 and its corollary also give



**Theorem 9.** The product of three symmetric orthogonal matrices  $A, B, C$  is also symmetric and orthogonal if, and only if, the scalar triple product  $[a, b, c]$  vanishes. (It is assumed that each of the three matrices is expressed in the form (3) above.)

In ordinary cartesian space this can be stated as follows:

The product of three reflections  $A, B, C$ , in planes  $\alpha, \beta, \gamma$ , respectively, is a reflection if, and only if,  $\alpha, \beta, \gamma$  have a line in common.

Suppose this condition is satisfied and the product is a reflection  $D$ . In the plane  $\pi$ , the points  $A, B, C, D$  will lie on a line meeting  $s$  in  $U, V$  such that  $(U, V), (A, C), (B, D)$  are in involution. Therefore

$$(UV, AB) = (VU, CD) = (UV, DC).$$

But  $(UV, AB) = e^{2i\theta}$  where  $\theta$  is the angle between the planes  $\alpha$  and  $\beta$ . [See e.g. Baker, 1928, whose terminology we follow here.] That is, if  $\beta$  is obtained from  $\alpha$  by rotation through an angle  $\theta$  then  $\delta$  is obtained from  $\gamma$  by rotation through  $-\theta$ .

**Rotations.** Any (non-singular) collineation  $R$  of the plane  $\pi$  which leaves  $s$  invariant induces a projectivity on  $s$  whose self-corresponding points are, say,  $U, V$ . Let us denote the line  $UV$  by  $l$  and the pole of  $l$  with respect to  $s$  by  $L$ . Since  $U$  and  $V$  are self-corresponding points of  $R$ , it follows that  $l$  is a self-corresponding line on which  $R$  induces a projectivity with  $U, V$  as the united points. The characteristic cross ratio of this projectivity is  $(UV, PP')$  where  $P$  is on  $l$  and  $P' = PR$ , and this cross ratio is independent of the choice of  $P$  on  $l$ . In cartesian space with origin  $O$ , the angle  $POP'$  ( $=\theta$ , say) is given by

$$2i\theta = \log (UV, PP'),$$

and  $OL$  is normal to the plane  $OL$ . It is therefore clear that the collineation  $R$  corresponds, in cartesian space, to a rotation about the vector  $l$  as axis through an angle  $\theta$ .

The lemma A preceding Theorem 3 yields

**Theorem 10.** Any orthogonal matrix can be factorised into the product of two symmetric orthogonal matrices, each of the form  $-\mathbf{I} + 2\mathbf{pp}'$ , and this can be done in  $\infty^1$  ways.

In ordinary cartesian space, we may say, with more detail:

Any rotation  $L$ , about an axis  $l$  through an angle  $\varphi$ , can be expressed as the product  $MN$  of two reflections, in planes  $\mu, \nu$ , respectively, say;  $\mu$  must be taken arbitrarily through  $l$  and  $\nu$  is then uniquely determined. (Or,  $\nu$  could be chosen arbitrarily and then  $\mu$  is uniquely determined.)

We will show further, now, that the angle between  $\mu$  and  $\nu$  is  $\frac{1}{2}\varphi$ .

Using the notation of Lemma A, let  $PN$  meet  $s$  in  $S$  and  $SQ$  meet  $UV$  in  $H$ . Therefore

$$L = MN = NH.$$

Now the pencil of conics through the points  $P, Q, R, S$  determine an involution on  $l$  in which  $(M, N), (U, V)$  are pairs and  $N$  is a double point; the other double point is  $G$ , the intersection of  $l$  with the polar of  $N$ . Therefore

$$ML = MMN = MN = H.$$

As  $M$  varies on  $l$ , the points  $M, N$  are in 1-1 correspondence in which  $U, V$  are the united points; also  $M \rightarrow N$  and  $N \rightarrow H$ . So

$$(UV, MN) = (UV, NH)$$

and hence

$$(UV, MH) = (UV, MN)^2.$$

It follows that the angle from  $\mu$  to  $\nu$  is  $\frac{1}{2}\varphi$ .

Theorem 3 now gives

*Theorem 11.* The product of reflections  $A, B, \dots, J, K$  (in planes  $\alpha, \beta, \dots, \kappa$ , say) is also a reflection if, and only if, the plane  $\kappa$  passes through the axis of the rotation defined by  $AB \dots J$ .

It should be noticed that this statement remains valid when  $AB \dots J$  is a reflection if we call the normal to the plane defining the reflection its "axis".

A purely algebraic formulation of this result may be conveniently given in terms of real matrices. A real orthogonal matrix  $R$ , if it is not symmetric, has one, and only one, real eigen vector which we shall denote by the corresponding lower case letter  $r$ . Let  $A, B, \dots, J, K$  be a set of real, symmetric, orthogonal (and, therefore, also involuntary) matrices; and also let  $AB \dots J = R$  where  $R$  is not symmetric. Then a necessary and sufficient condition that  $AB \dots JK$  be symmetric is  $r'k=0$ . If  $R$  is symmetric, but is not the identity, the above condition is still valid provided  $r$  is taken to be that eigen vector of  $R$  which is uniquely determined, i.e.  $r$  is the normal to the plane defining the reflection  $R$ . The case  $R=I$  is trivial.

*Vector Form for Rotations.* The above results enable us to obtain vector forms for a rotation and for the composition of two rotations, the axis of a rotation being specified by a unit vector and the angle by a scalar.

Every real, proper, orthogonal matrix  $A$  is of the form  $e^Q$  where  $Q$  is skew-symmetric [Taber, 1892]. Suppose

$$Q = \begin{pmatrix} 0 & -q_3 & q_2 \\ q_3 & 0 & -q_1 \\ -q_2 & q_1 & 0 \end{pmatrix},$$

where the  $q_i$  are real numbers, not all zero. The characteristic equation of  $Q$  is

$$\lambda^3 + (q_1^2 + q_2^2 + q_3^2)\lambda = 0,$$

so that we have, by the Hamilton-Cayley theorem,

$$Q^3 = -q^2 Q,$$

where  $q' = (q_1, q_2, q_3)$  and  $q = |q|$ .

Writing  $Q = qS$ , then

$$S = \begin{pmatrix} 0 & -s_3 & s_2 \\ s_3 & 0 & -s_1 \\ -s_2 & s_1 & 0 \end{pmatrix},$$

where  $s_i = q_i/q$ ; thus the vector defined by  $s' = (s_1, s_2, s_3)$  is a unit vector. We now have  $S^3 = -S$  and therefore

$$\begin{aligned} A &= e^Q = e^{qS} \\ &= I + qS + \frac{q^2 S^2}{2!} - \frac{q^3 S}{3!} - \frac{q^3 S^2}{4!} + \dots \\ &= I + \sin qS + (1 - \cos q)S^2 \end{aligned} \quad (4)$$

Now  $Ss = s \times s = O$  and therefore  $S^2 s = O$ .

Hence  $As = s$  and it follows that  $s$  is the axis of the rotation  $A$  defined by  $A$ .

Let the angle of rotation of  $A$  be  $\theta$ , so that  $A$  is fully and uniquely determined by  $s$  and  $\theta$ . Regarding  $s$ , and therefore  $S$ , as fixed, we may write

$$f(\theta) = A = e^{qS} = I + \sin qS + (1 - \cos q)S^2 \quad (5)$$

where  $q$  is some function of  $\theta$ . For any integer  $n$  we have

$$f(n\theta) = A^n = e^{nqS} = I + \sin nqS + (1 - \cos nq)S^2, \quad (6)$$

and, in fact, this holds for any rational number  $n$ . It can now be readily shown that  $q \equiv \theta \pmod{2\pi}$ . Therefore, the rotation has matrix

$$A = e^{\theta S} = I + \sin \theta S + (1 - \cos \theta) S^2,$$

and hence, for any vector  $\mathbf{x}$ ,

$$A\mathbf{x} = \mathbf{Ax} = \mathbf{x} + \sin \theta \mathbf{s} \times \mathbf{x} + (1 - \cos \theta) \mathbf{s} \times (\mathbf{s} \times \mathbf{x}), \quad (7)$$

since  $S\mathbf{x} = \mathbf{s} \times \mathbf{x}$  and  $S^2\mathbf{x} = S(S\mathbf{x}) = \mathbf{s} \times (\mathbf{s} \times \mathbf{x})$ .

Now let  $A, B$  be two rotations about axes  $\mathbf{a}, \mathbf{b}$  (unit vectors) through angles  $2\theta, 2\varphi$ , respectively. In the plane at infinity, let  $A, B$  be the points of coordinate vectors  $\mathbf{a}, \mathbf{b}$ , and let their polars, with respect to  $s$ , be  $\lambda, \mu$ , respectively; also denote the point  $(\lambda, \mu)$  by  $N$ ;  $N$  is therefore the pole of  $AB$  and we may take  $\sin \gamma \mathbf{n} = \mathbf{a} \times \mathbf{b}$ . By Theorem 10, there exists a point  $M$  on  $\lambda$  and a point  $L$  on  $\mu$  such that

$$A = MN \text{ and } B = NL.$$

Hence  $AB = ML$ . Denoting the pole of  $ML$  by  $C$  (given by a unit vector  $\mathbf{c}$ ) and the interval  $ML$  by  $\psi$  we see that  $AB$  is a rotation  $C$  about the axis  $\mathbf{c}$  through the angle  $2\psi$ . It follows from Theorem 10 that  $M \rightarrow N$  by a rotation about  $\mathbf{a}$  through angle  $\theta$ , and so we have, using (7),

$$\begin{aligned} \mathbf{m} &= \mathbf{n} - \sin \theta \mathbf{a} \times \mathbf{n} + (1 - \cos \theta) \mathbf{a} \times (\mathbf{a} \times \mathbf{n}). \\ &= \cos \theta \mathbf{n} - \sin \theta \mathbf{a} \times \mathbf{n}. \end{aligned}$$

Similarly,

$$\mathbf{l} = \cos \varphi \mathbf{n} + \sin \varphi \mathbf{b} \times \mathbf{n}.$$

Therefore  $\cos \psi = \mathbf{l} \cdot \mathbf{m} = \cos \theta \cos \varphi - \sin \theta \sin \varphi (\mathbf{a} \times \mathbf{n}) \cdot (\mathbf{b} \times \mathbf{n})$   
 $= \cos \theta \cos \varphi - \sin \theta \sin \varphi \cos \gamma.$

where  $\cos \gamma = \mathbf{a} \cdot \mathbf{b}$ , and so we have obtained an expression for the angle  $2\psi$  of the resultant rotation  $C$ .

To find the axis of  $C$  we have

$$\begin{aligned} \mathbf{m} \times \mathbf{l} &= (\sin \theta \cos \varphi) \mathbf{a} + (\cos \theta \sin \varphi) \mathbf{b} - \sin \theta \sin \varphi (\mathbf{a} \times \mathbf{n}) \times (\mathbf{b} \times \mathbf{n}) \\ &= (\sin \theta \cos \varphi) \mathbf{a} + (\cos \theta \sin \varphi) \mathbf{b} - (\sin \theta \sin \varphi) \mathbf{a} \times \mathbf{b}. \end{aligned}$$

The axis  $\mathbf{c}$  of  $C$  is parallel to  $\mathbf{m} \times \mathbf{l}$  and is therefore determined.

If we write  $\mathbf{a}_1 = \tan \theta \mathbf{a}$ ,  $\mathbf{b}_1 = \tan \varphi \mathbf{b}$  then  $\mathbf{c}$  is parallel to the vector  $\mathbf{a}_1 + \mathbf{b}_1 - \mathbf{a}_1 \times \mathbf{b}_1$ .

#### ACKNOWLEDGEMENTS.

I wish to thank Professor T. G. Room for helpful suggestions in the preparation of this paper.

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## NATURE AND OCCURRENCE OF PEAT AT HAZELBROOK, NEW SOUTH WALES.

By J. A. DULHUNTY, D.Sc.

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### OCCURRENCE AND ORIGIN.

Small lenses of well-preserved peat occur at depths of 5 to 6 feet in sandy soil about one mile north-west of Hazelbrook in the Blue Mountains. The material is of considerable interest owing to its unusual mode of occurrence and origin, and its significance in relation to early stages of coalification.

High-humus soils are common on elevated country, between 2000 and 4000 feet above sea level in the Eastern Highlands of New South Wales, but true peat has not formed as climatic conditions were not suitable during late Tertiary and Pleistocene time. In the Southern Highlands of New South Wales peat is accumulating at isolated places above 6000 feet on the Kosciusko Plateau, but alpine conditions in that area are quite different from those in any other part of New South Wales. In view of this, the occurrence of true peat at Hazelbrook (1000 feet above sea level) was investigated with the object of explaining its presence where climatic conditions have not been suitable for normal peat-formation.

The peat occurs as irregular lenses, up to 1 inch in thickness and 3 feet in diameter, distributed sporadically at the base of about 6 feet of sandy soil which lies on soft, partly weathered Hawkesbury Sandstone (Triassic) in a relatively mature valley of late Tertiary or early Pleistocene age. The sandy soil becomes more compact as it passes downwards from the surface. It also contains pebbly layers and horizons of ferruginous concretions which are typical of the underlying and surrounding beds of Triassic sandstone. The sandstone contains an argillaceous cement and relatively deep weathering or softening is common on old surfaces from which sand and clay have not been washed away. The pebbly layers and horizons of ferruginous concretions, in the sandy soil above the peat, lie parallel to the bedding of the underlying sandstone rather than the surface. This strongly suggests that the soil represents weathered or softened sandstone rather than recently transported alluvium.

From the nature of occurrence, outlined above, it appears evident that the peat is embedded in weathered Triassic sandstone, which presents an unusual problem as the peat has suffered very little compression and, from its general nature and properties, it is certainly much younger than the sandstone. At all other places plant material embedded in the Hawkesbury Sandstone during deposition is now in the form of hard bright coal of bituminous rank.

A possible explanation of the origin of the peat is suggested by the behaviour of roots of contemporary plants growing in the sandy soil above the peat. The partly weathered sandstone immediately beneath the peat appears to be a harder bed which has resisted weathering more than the overlying material. Roots of contemporary plants have found their way down through the completely softened sandstone and some have penetrated the peat lenses, but they have not entered the partly weathered sandstone underlying the peat. This suggests that the peat may have been formed by roots penetrating to the partly weathered

sandstone bed and spreading out to form "root mats" over a long period of time. Root material first introduced into the weathered sandstone in this way could have been preserved as a result of anaerobic conditions prevailing beneath ground-water level. With time, more roots probably entered the small root mats to become preserved after death, and thus add to the bulk of organic material in the peat lenses. Such a process would explain the occurrence of Pleistocene peat in weathered Triassic sandstone, and also the preservation of plant material to form peat in an area where climatic conditions have not been suitable for preservation at the surface in the normal manner.

The mode of origin outlined above was suggested after geological examination of the occurrence, and it was evident that if the peat had been formed in that way it would not contain pollen, spores or those parts of plants which extend above the surface of the ground. If, however, it had been deposited at the surface and subsequently buried it would be certain to contain aerial plant remains. In view of this, samples of the peat were submitted to Mr. J. Waterhouse, Department of Botany, University of Sydney, for microscopical examination with the object of obtaining further evidence relating to the nature of the material and its origin. His conclusions were as follows:

"Macroscopically, there appear to be roots in various stages of disintegration ramifying throughout the material. It was difficult to section the peat for microscopic study as it did not respond favourably to the usual procedure of wax-embedding. However, sections which were obtained exhibited normal root structures and revealed among the débris bodies that appear to be vesicles and subtending hyphæ of vesicular-arbuscular mycorrhizal fungi which normally occur associated with roots of some plants. No pollen grains were observed. The examination would therefore suggest that the peat has not originated from surface material, but rather that it was formed by accumulation of root material."

The foregoing results support conclusions based on geological evidence that the peat represents an accumulation of root material at some depth beneath the surface where it was preserved under anaerobic conditions below ground-water level. It follows that the occurrence does not necessarily indicate the recent existence of climatic conditions normally required for the formation of peat.

#### NATURE AND PROPERTIES.

The peat consists of soft fibrous root fragments, up to 8 inches in length and about  $\frac{1}{4}$  inch in diameter, set in a matrix of finely divided root material and a stiff structureless gel-like substance. As a whole the peat is firm and compact but can be easily cut with a knife, and it is of a somewhat springy or rubbery nature when pressed or bent by hand. When taken from the moist sandy soil in which it occurs, the peat can be preserved in its original condition by storing in a closed jar. It also retains its original condition if placed over water in a closed jar, but when actually immersed it takes up, or absorbs, large amounts of water and swells to several times its original volume. When air-dried, the peat shrinks to about one-half its volume and becomes hard and brittle, but if immersed in water it readily takes up moisture and returns to its original condition. This property indicates that it has not reached the state of maturity, with respect to development of colloidal or micelle structure, at which irreversible physical changes occur when water is removed by drying (Dulhunty, 1946 and 1949).

For the purpose of chemical analysis and determination of maximum inherent moisture the peat was separated by hand into three components: A, Large pieces of root material. B, That portion of the peat which consisted mainly of finely divided fibrous material and a small amount of gel-like substance. C, The gel-like substance with very little fibrous material. Ultimate and proximate analyses were carried out on the three components, and values for

maximum inherent moisture were determined by Controlled Vaporisation of Adherent Moisture (for details of process see Dulhunty, 1947). Results of analyses and moisture values, shown in Table I, indicate that components A and B are very similar with respect to carbon, hydrogen and moisture, but ash and volatiles are considerably lower in A. Component C is lower in carbon but somewhat higher in hydrogen and moisture than components A and B.

TABLE I.  
*Analytical Data and Moisture Properties of Components in Hazelbrook Peat.*

Peat Com- ponent.	Percentage Ash-free Dry Peat.				Percentage Dry Peat.	
	Carbon.	Hydrogen.	Vols.	Fixed Carbon.	Maximum Inherent Moisture.	Ash.
A	53.10	5.22	66.7	33.3	40.31	2.74
B	54.08	5.62	78.1	21.9	40.12	8.90
C	47.3	5.88	76.1	23.9	56.00	6.80

Component A, large pieces of root material, would appear to be the precursor of vitrain in higher rank coal, whilst component B, consisting of more finely divided fibrous material together with some of the gel-like substance, would probably become a canneloid clarain if coalification were to continue to bituminous rank. The low carbon content and high moisture value of the structureless gel-like substance, component C, suggest that it is some form of humic degradation product derived by limited biological decay of the root material. This substance probably represents the peat-stage or precursor of a homogeneous structureless cannel-coal constituent with unusually low hydrogen content and volatile yield owing to the complete absence of spores, cuticle and resin, which normally characterise cannel derived from surface plant-material.

The carbon contents and volatile yields of components A and B indicate that the peat is very immature with respect to chemical rank as changes have advanced only a little beyond the average composition of wood which contains about 50% carbon and yields about 80% volatiles. The small change which has taken place is evidently associated with the biological processes of preliminary decay followed by preservation under more or less anaerobic conditions.

Relationships between maximum inherent moisture and rank or carbon content, for vitrains of all rank from peat to anthracite, were recently investigated (Dulhunty, 1948). It was shown that in the peat stage the woody precursors of vitrain, with 55% to 60% carbon, have moisture values of 30% to 50%. As rank increases moisture rises to between 70% and 120% at brown-coal rank (carbon about 70%), where it reaches a maximum in the carbon-moisture relationship. With further increase in rank, moisture then falls to less than 5% at the well-known minimum at high-rank bituminous stage. In the case of the woody constituents, components A and B, in the Hazelbrook peat, the moisture values of about 40% for 53% to 54% carbon are in keeping with the general relationship established for the woody constituents of peats formed in the normal manner. The relatively low moisture values of about 40% indicate that the woody constituents of the Hazelbrook peat are very immature with respect to physical rank as well as chemical rank, and it is probable that much of the original physical structure of cellulose and lignin still remains, and that only a

limited amount of the true gel, or colloidal structure, of higher-rank peats and brown coals has developed. The somewhat higher moisture value of 56% for the gel-like substance, with 47.3% carbon suggests that its physical rank is in advance of its chemical rank, and that practically all the original ultra-fine structures of the plant materials have been replaced by the colloidal structures which represent the first stages in the formation of the micelle structures in higher-rank coals. This accounts for the springy or rubbery nature of the peat.

When carbon content reaches about 60%, and maximum inherent moisture rises to between 60% and 70%, low-rank coals reach the stage at which irreversible physical changes occur on drying (Dulhunty, 1948). At this stage it is believed that the ultra-fine structure consists essentially of well-developed micelles, the majority of which are just touching with very small contact points. The Hazelbrook peat has not yet attained this rank-stage, with respect to either physical or chemical rank. It is probable that its ultra-fine structure, in addition to residues of the original cellulose and lignin structure, consists mainly of "primary units" (Bangham, 1943), which eventually segregate to form micelles, dispersed in a watery medium. This degree of colloidal development, with the absence of micelles touching at contact points, would explain the fact that the peat can be dried and resaturated without causing permanent change in its ultra-fine structure. Also the condition of component C, which appears to consist almost entirely of unsegregated primary units dispersed in a watery medium, would account for the fact that the peat takes up water and swells to several times its original volume if immersed after removal from its place of occurrence where it is confined under slight pressure from the weight of overlying sand.

In general, it appears that the Hazelbrook material is a true but immature peat in which plant constituents have been partly changed to humic products representing the first step in the building of the complex "coal molecule", and that the material is in the earliest stages of the process of physical development which eventually gives rise to the well-organised micelle structure of coal. It is believed that further study of the physical and organic chemistry of such peats may provide important data and contribute towards a better understanding of the mechanism by means of which plant material is changed to coal.

#### ACKNOWLEDGEMENTS.

In conclusion, the writer wishes to thank Mr. A. G. Bourne, of Hazelbrook, for drawing his attention to the occurrence of peat in the locality. It is also wished to acknowledge the assistance of Mr. J. Waterhouse in botanical examination of the peat; laboratory work by Misses Nora Hinder and Ruth Penrose; and facilities provided by the Commonwealth Research Grant to the University of Sydney.

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## THE RESOLUTION OF THE TRIS o-PHENANTHROLINE NICKEL II ION.

By F. P. DWYER, D.Sc.,  
and (Miss) E. C. GYARFAS, M.Sc.

*Manuscript received, October 13, 1949. Read, December 7, 1949.*

When excess of o-phenanthroline is added to a nickel salt solution, pink coloured compounds result which have been shown to have the constitution  $\text{Ni(phenan)}_3\text{X}_2 \cdot n\text{H}_2\text{O}$  (Pfeiffer and Tappermann, 1933). These substances are analogous to the tris 2:2' dipyridyl compounds  $\text{Ni(dipy)}_3\text{X}_2 \cdot n\text{H}_2\text{O}$  which are also pink and have been resolved into enantiomorphous forms (Morgan and Burstall, 1931). With two molecules of phenanthroline to one of nickel salt, blue compounds may be isolated (Pfeiffer and Tappermann, *loc. cit.*), of the composition  $\text{Ni(phenan)}_2\text{X}_2 \cdot n\text{H}_2\text{O}$ . Whether these compounds are the octahedral complexes  $[\text{Ni(phenan)}_2\text{H}_2\text{O}]\text{X}_2 \cdot (n-2)\text{H}_2\text{O}$  or simply hydrated 4-covalent complexes is unknown, but analogy with the hexammine and tetrammine series of nickel compounds supports the latter interpretation.

In the present communication the resolution of the tris o-phenanthroline nickel ion is described and also experiments carried out in an effort to resolve the blue bis compounds. The resolution of the tris-phenanthroline nickel ion was achieved by the addition of an excess of potassium d-antimonyl tartrate to a solution of the complex chloride, when the d-tris o-phenanthroline nickel d-antimonyl tartrate separated as a highly insoluble crystalline precipitate. The optically active acid was eliminated by the addition of alkali, and the active nickel complex precipitated as the sparingly soluble perchlorate. The laevo form was obtained from the filtrate by precipitation with sodium perchlorate solution. The active perchlorates were purified by recrystallisation from warm aqueous acetone, the d,l perchlorate impurity separating as the least soluble fraction.

The optical forms were much more stable than the active forms of the tris 2:2' dipyridyl nickel ion. Thus, whilst Morgan and Burstall (*loc. cit.*) found that solutions of the active form of this substance racemised completely in  $1\frac{1}{2}$  hours at  $20^\circ\text{C}$ ., the phenanthroline complexes had lost only 50% of the activity in 18 hours, and at the end of  $73\frac{1}{2}$  hours still possessed a slight rotation. An unexpected observation was that the racemisation rate was reduced in the presence of sulphuric acid. This effect is being studied in detail in order to gain information of the mechanism of racemisation.

Like the corresponding ruthenium compound  $\text{Ru(phenan)}_3(\text{ClO}_4)_2$ , whose resolution has been described previously (Dwyer and Gyarfás, 1949), when examined in the wavelengths 589.0 and 546.1  $\mu$ , the nickel compound showed a large abnormal rotatory dispersion. The absorption and rotatory dispersion curves will be described in a subsequent communication.

When the blue solutions containing the biso-phenanthroline complex were treated with potassium antimonyl tartrate, pale pink precipitates of the tris phenanthroline complex were obtained even when the ratio of nickel to the base was only 1:1.5, suggesting that the bis complex was in equilibrium with the tris complex





This observation was confirmed by the precipitation of  $\text{Ni}(\text{phenan})_3(\text{ClO}_4)_2$  from blue solutions, which had been boiled to ensure that any of the tris compound, accidentally prepared by a local high concentration of phenanthroline during the preparation of the bis compound should be transformed. The ease of change of the bis complex to the tris obviates all possibility of resolution.

### EXPERIMENTAL.

A 4 dm. tube was used for all measurements of rotation.

#### *d-Tris o-Phenanthroline Nickel d Antimonyl Tartrate.*

d,l Tris o-phenanthroline nickel chloride was prepared as described by Pfeiffer and Tappermann (*loc. cit.*), by the addition of finely divided o-phenanthroline monohydrate (3.0 g.) to a solution of nickel chloride hexahydrate (1.2 g.) in water (100 mls.). The mixture was stirred until the phenanthroline had dissolved completely, and to the resulting red solution was added slowly a solution of potassium antimonyl tartrate (4.8 g.—3 mols.) in water (30 mls.). On scratching the sides of the vessel, a pink crystalline precipitate was obtained. The solution was cooled rapidly from room temperature to approximately 5° C. in ice and filtered. The precipitate was washed with ice water and purified by solution in 0.1 N caustic soda (50 mls.) and after filtration, precipitated by the addition of acetic acid and a little potassium antimonyl tartrate. The pure substance crystallised in pale pink needles.

A 0.02% solution in N/100 sodium hydroxide gave  $\alpha = +0.76^\circ$ ; whence  $[\alpha]_D^{15} = +950^\circ$ .

Found: N=6.45%; Sb=18.79%.

Calculated for  $[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3] \cdot [\text{SbO}_4\text{C}_4\text{H}_4\text{O}_6] \cdot 2.7\text{H}_2\text{O}$ : N=6.49%; Sb=18.79%.

#### *d,l-Tris o-Phenanthroline Nickel Perchlorate Dihydrate.*

The inactive perchlorate prepared by the addition of sodium perchlorate solution to a solution of the inactive chloride gave pink rectangular prisms from hot aqueous acetone. The compound was very sparingly soluble in water.

Found: Ni=7.040%.

Calculated for  $[\text{Ni}(\text{CH}_6\text{N}_2)_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ : Ni=7.036%.

#### *d-Tris o-Phenanthroline Nickel Perchlorate Trihydrate.*

The d tris o-phenanthroline nickel d-antimonyl tartrate was dissolved in approximately N/20 caustic soda (50 mls.) by shaking at room temperature and the solution filtered. Sodium perchlorate solution was then added drop by drop, with scratching of the sides of the vessel when the d- perchlorate precipitated in pale pink micro crystals. After washing with ice water, the precipitate was dissolved in warm 30% acetone in water, and fractionally precipitated with sodium perchlorate. The first fraction was discarded and the more soluble fractions combined and recrystallised from aqueous acetone by the addition of sodium perchlorate. The substance crystallised in flat pink plates and was appreciably soluble in cold water to give a pink solution. A 0.02% solution in water gave  $\alpha_D = +1.17^\circ$  and  $\alpha_{5461} = +1.39^\circ$ , whence  $[\alpha]_D^{15} = +1463^\circ$  and  $[\alpha]_{5461}^{15} = +1738^\circ$ ; or  $[\text{M}]_D^{15} = +12,470^\circ$  and  $[\text{M}]_{5461}^{15} = +14,810^\circ$ .

Found: Ni=6.85%; N=9.25%.

Calculated for  $[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ : Ni=6.89%; N=9.23%.

#### *l-Tris o-Phenanthroline Nickel Perchlorate Trihydrate.*

The residual solution after the precipitation with potassium antimonyl tartrate was strongly laevo rotatory and was treated carefully with sodium perchlorate solution, avoiding an excess to prevent the precipitation of potassium perchlorate. Alternatively it was treated with sodium iodide solution and the insoluble iodide dissolved in aqueous acetone and then precipitated as the perchlorate. The perchlorate precipitate was recrystallised as for the d form above, and gave flat pink plates of the pure laevo perchlorate. Occasionally this substance appeared in a yellow

dimorphous form if the aqueous acetone solution was too hot. The yellow form gave a pink solution in water and had the same rotation as the pink form.

A 0.02% solution in water gave  $\alpha_D = -1.17^\circ$  and  $\alpha_{5461} = -1.39^\circ$ , whence  $[\alpha]_D^{15} = -1463^\circ$  and  $[\alpha]_{5461}^{15} = -1738^\circ$ ; or  $[M]_D^{15} = -12,470^\circ$  and  $[M]_{5461}^{15} = -14,810^\circ$ .

Found: Ni=6.89%; N=9.21%.

Calculated for  $[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ : Ni=6.89%; N=9.23%.

#### SUMMARY.

Tris o-phenanthroline nickel perchlorate has been resolved through the antimonyl tartrate. The optical forms were much more stable than those of the tris 2:2' dipyridyl nickel ion, and showed a large abnormal rotatory dispersion.

#### ACKNOWLEDGEMENTS.

The authors are indebted to Miss J. Fildes for microanalyses (N), and one of us (E.C.G.) is indebted to the Commonwealth Research Committee for an Assistantship.

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## A NOTE ON THE REACTION BETWEEN CHROMIUM II SALTS AND o-PHENANTHROLINE.

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Edmonds, Hammett and Chapman (1934) by the reaction between chromous acetate and o-phenanthroline obtained a red solution, which was oxidisable to a purplish red colour. The potential of the reaction, which was reversible, was found to be approximately +0.77 volt, but because of the poor colour intensity and the unsuitable colour change the substance was considered valueless as a redox indicator. The original reddish coloured solution was claimed to contain tris o-phenanthroline chromium II acetate and the oxidation reaction to be



The substance responsible for the colour was not isolated and no analyses are available. The present note deals with attempts to isolate tris o-phenanthroline chromium II salts with a view to their systematic investigation and possible resolution.

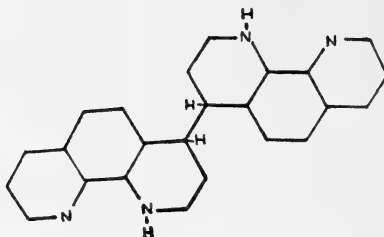
Chromous acetate, or better, chromous chloride or sulphate, was found to react with phenanthroline with the production of reddish solutions, which yielded orange amorphous precipitates with chloride or sulphate ion. The filtrates from the precipitations were still coloured and gave reddish crystalline precipitates with iodides and perchlorates. The amorphous precipitates were oxidisable with ceric and dichromate to the purple coloured solutions, but the red crystalline iodides and perchlorates were not.

The orange amorphous precipitates were nearly insoluble in water and the usual organic solvents, but dissolved easily in dilute acids on warming and reprecipitated in the amorphous condition on cooling or dilution. As originally prepared, the amorphous substances contained C, H, N, S and Cr, but after purification by repeated solution in acid and reprecipitation the chromium was lost but the substances, now an orange yellow colour, were still oxidisable with potassium dichromate to a purple colour which was destroyed reversibly by reducing agents.

The red crystalline iodides and perchlorates also contained organic matter and chromium, but were not oxidisable and appeared to be impure compounds of chromium III and phenanthroline. These substances which are the chromium analogues of the ferric phenanthroline compounds,  $[\text{Fe(phenan)}_2\text{OH}]_2\text{X}_4$  (Gaines, Hammett and Walden, 1936), will be described in a subsequent communication.

It thus appears that the reaction between phenanthroline and chromium II salts yields a mixture of products, and the oxidisable substance is not a chromium II compound but a reduction product of o-phenanthroline. This observation was confirmed by reducing o-phenanthroline by a variety of methods in the absence of chromium salts. The reducing agents included zinc and hydrochloric acid, zinc-amalgam and sulphuric acid, sodium amalgam, sodium in alcohol, at a mercury surface polarographically and cathodically with a lead electrode. Cathodic reduction appeared the best method of obtaining the

reduction products free from metallic impurities. The reduced solutions were orange to orange red in colour and were reversibly oxidisable. They contained at least two substances, one of which was oxidisable and the other not. One of these substances isolated as the iodide was pale yellow, non-oxidisable and had the formula  $C_{12}H_9N_2.HI$ . A possible structure is



This substance appears to be the first product of reduction of phenanthroline, further reduction leading to the oxidisable material which has not been isolated pure.

Preliminary experiments on the reduction of *o*-phenanthroline polarographically (Breyer, Buchanan and Casimir, 1948) indicate that two steps are involved, the first of one electron and the second of three.

### EXPERIMENTAL.

#### *The Reaction between Chromium II Salts and o-Phenanthroline.*

Chromium III chloride hexahydrate was reduced in hydrochloric acid solution with zinc amalgam until a blue colour resulted. Solid sodium acetate was added and the red crystalline chromium II acetate was filtered in an atmosphere of carbon dioxide. The solid acetate was added directly to oxygen-free solutions of *o*-phenanthroline acetate, or alternatively dissolved in 0.5 N sulphuric or hydrochloric acids and added to solutions of the base in aqueous alcohol. In all experiments red solutions resulted which yielded orange precipitates with chloride, sulphate, iodide or perchlorate.

All of the precipitates were reversibly oxidisable with potassium dichromate, or permanganate, bromine water and ceric salts.

With chromous sulphate good yields of the orange substance were obtained by the subsequent addition of sodium sulphate. After washing and drying the substance gave: C=43.84%; H=3.84%; N=7.93%; Cr=7.73%; (S not estimated); and after solution in sulphuric acid and reprecipitation with water: C=56.06%; H=4.98%; N=9.50%; Cr=2.03. With further purification the chromium was finally eliminated. The analytical figures did not agree with any possible compound, and it was concluded that the substance was an inseparable mixture.

#### *The Cathodic Reduction of o-Phenanthroline.*

The base 0.5 g. in sulphuric acid (50 cc., 1 N) was reduced at a lead cathode in a small beaker separated from the anode by the membrane of a sintered glass crucible. Current density=0.02 amp./sq. dm.; time=3 hours. The solution became pale orange and was finally evaporated to half its volume. After filtration from a small amount of orange precipitate, potassium iodide was added. The reddish precipitate was crystallised from hot water, leaving a red material insoluble, and gave large translucent yellow crystals, m.p. 200–202° C. This substance was not oxidisable.

Found: C=46.23%; H=3.38%; N=8.63%; I=41.0%.

Calculated for  $C_{12}H_9N_2.HI$ : C=46.46%; H=3.55%; N=9.03%; I=40.94%.

With longer reduction the solutions became orange red, and gave precipitates with iodides and perchlorates which were oxidisable. A base could be liberated with sodium carbonate. This substance melted above  $300^{\circ}\text{C}$ ., and was highly insoluble except in acids. Despite many attempts analytically pure specimens could not be isolated and the structure of the oxidisable substance is still unknown.

*The Potentiometric Oxidation of the Reduction Product.*

The material for these measurements was made by reduction with chromous salts or cathodically. The curves obtained, which showed only one break, were identical and within the limits of experimental error gave the same value for the redox potential.

The reaction was carried out at  $0^{\circ}\text{C}$ . to increase the stability of the oxidised product and the measurements were made as quickly as possible. The titrating agent was ceric sulphate, the electrode smooth platinum foil, and the redox potentials shown in Table I were estimated from the half titration value.

TABLE I.

Acid Concentration.	Potential. (Volts.)
$\text{H}_2\text{SO}_4$ .	
10 N	0.90
7 N	0.88
5 N	0.87
3 N	0.86
2 N	0.86

On standing the purple colour was gradually discharged, but could be regenerated by the addition of more of the oxidising agent.

SUMMARY.

The reaction between chromium II salts and o-phenanthroline has been found to yield not complex chromium II compounds but a mixture of orange reduction products, one of which can be oxidised to a purple substance. The reduction could also be effected cathodically and by strong reducing agents such as zinc and acid. One of the reduction products isolated as the hydriodide had the formula  $\text{C}_{12}\text{H}_9\text{N}_2\cdot\text{HI}$ , but was not oxidisable. The redox potential of the oxidisable material was approximately  $+0.87$  volt.

ACKNOWLEDGEMENTS.

The authors are indebted to Miss J. Fildes for microanalyses and Miss E. C. Gyrfas for assistance with the potentiometric titrations.

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# DETERMINATION OF THE BOILING POINTS OF AQUEOUS NITRIC ACID.

By L. M. SIMMONS, B.Sc., Ph.D., F.A.C.I., A.R.I.C.,  
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With two text-figures and three tables.

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Inconsistencies in the published boiling points of aqueous hydrogen chloride solutions led to the design of a static method for rapidly determining the boiling points of pure and mixed liquids which do not attack mercury, glass or tap lubricant (Simmons, 1945). The method was later developed to eliminate the tap lubricant (Simmons, 1947), and the present further adaptation described herein enables the method to be used with liquids which attack mercury, such as aqueous nitric acid.

As was the case for aqueous hydrogen chloride solutions, the boiling points of aqueous nitric acid have hitherto been determined by dynamic methods, and these are known to suffer from two important sources of error, viz. superheating and change in concentration during the distillation of all samples except the azeotropic solution. The boiling points of aqueous nitric acid given in the International Critical Tables are based on the observations of Creighton and Githens (1915) using a dynamic method due to Young (1902). Although Young claimed that with the large quantity of liquid present and the small flame that is required, there is no fear of the vapour being superheated, he later stated in his monograph (1922) that "the boiling point of a liquid can only be correctly determined by observing the temperature of the liquid itself under such conditions that ebullition is impossible". This latter view is in accord with the conclusion arrived at by Swietoslawski (1945).

Table I shows the values published at various times for the boiling point and composition of the constant boiling mixture of water and nitric acid at or near standard pressure.

TABLE I.  
*Boiling Point and Composition of Constant Boiling Aqueous Nitric Acid.*

Date.	Observed by.	Pressure. (Millimetres Mercury.)	B.p. (° C.)	Percentage HNO <sub>3</sub> by Weight.	Remarks.
Before 1861	Dalton <i>et al.</i>	Not stated	120	66-70	Reported by Roscoe, 1861.
1861	Roscoe.	735	120·5	68·0	
1915	Creighton and Githens.	760	121·7- 121·8	68·18- 69·24	
1928	—	760	121·9	67·3	International Critical Tables.
1949	Simmons and Canny.	760±0·5	120·6±0·2	67·5±0·5	Present investigation.

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## RESULTS.

The boiling points found for aqueous nitric acid solutions at 760 mm. by the present method are shown by curve A (Fig. 1).

That portion of curve A which represents solutions containing more than 78 per cent. by weight of  $\text{HNO}_3$  is dotted in order to indicate that decomposition

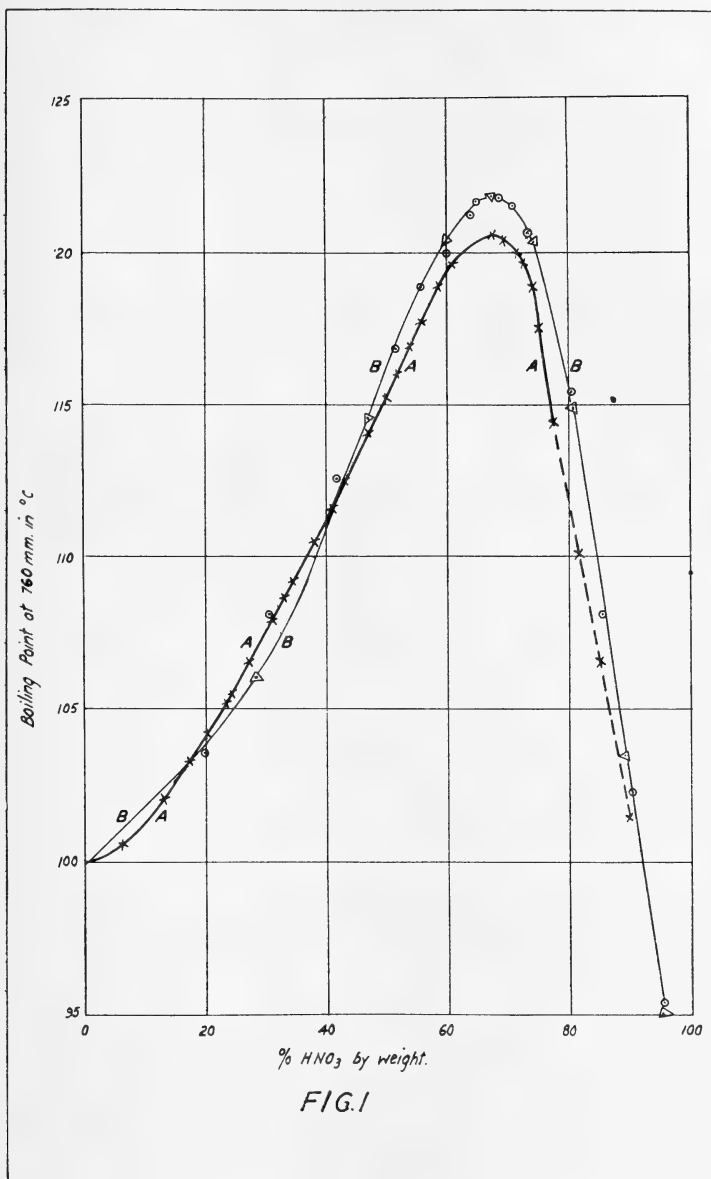


Fig. 1.—The Boiling Points of Aqueous Nitric Acid.

- A. According to the present investigation, observations plotted thus:  $\times$ .  
 B. According to the International Critical Tables. Tabulated values plotted thus:  $\Delta$ .  
 Creighton and Githens' observations plotted thus:  $\odot$ .

takes place before the normal boiling points are reached. In such circumstances a normal boiling point cannot strictly be quoted, for the apparent boiling point would be affected by the rate of heating, the presence of light and of catalysts, and by other factors which may affect the rate of decomposition.

The data from which curve A was plotted is given in Table II.

TABLE II.

*The Boiling Points of Aqueous Nitric Acid Containing Various Percentages by Weight of  $\text{HNO}_3$  at a Pressure of 760 mm.*

Percentage $\text{HNO}_3$ by Weight.	B.p. ( $^{\circ}\text{C}.$ )	Percentage $\text{HNO}_3$ by Weight.	B.p. ( $^{\circ}\text{C}.$ )	Percentage $\text{HNO}_3$ by Weight.	B.p. ( $^{\circ}\text{C}.$ )
0.0	100.0	37.9	110.5	69.2	120.4
6.1	100.6	41.0	111.7	71.7	120.0
12.9	102.1	43.0	112.5	72.2	119.7
17.0	103.3	47.3	114.1	73.7	118.9
20.3	104.2	49.7	115.2	75.3	117.6
23.3	105.2	52.0	116.0	77.4	114.4 <i>d.</i>
24.0	105.6	53.6	117.0	82.1	110.1 <i>d.</i>
27.2	106.6	56.0	117.7	85.6	106.6 <i>d.</i>
31.0	107.9	58.5	118.9	89.6	101.5 <i>d.</i>
32.7	108.7	62.0	119.6		
34.5	109.2	67.5	120.6		

*d* means that the sample decomposed at its boiling point.

For the purpose of comparison, Fig. 1 also shows a curve B, drawn according to the data given in the International Critical Tables. On this curve points marked  $\triangle$  indicate the International Critical Tables data, while points marked  $\odot$  show the observations listed by Creighton and Githens.

It will be seen that the boiling point of the constant boiling mixture is listed by the International Critical Tables as more than a centigrade degree higher than that found by the present method. It is of interest to recall that the same tables quote a maximum boiling point for hydrochloric acid more than a centigrade degree higher than that found by Simmons (1945) in confirmation of the measurements made by Bonner and Wallace (1930).

Table III is therefore submitted to replace that given on page 309 of Volume 3 of the First Edition of the International Critical Tables.

TABLE III.

B = $\text{HNO}_3$ .		
B.p. ( $^{\circ}\text{C}.$ )	M % B.	
	760 mm.	
100.0		0
106.9		10
113.9		20
119.2		30
<b>120.6</b>		<b>37.2</b>
118.7		45
111.3		55
105.2		65
102.2		70

The last three entries in Table III refer to temperatures at which decomposition accompanies boiling.



## APPARATUS AND PROCEDURE.

The J-tube shown in Fig. 2 is made of soda-glass and has an internal bore of about 7 mm. The length of the longer limb is about 20 cm.; that of the

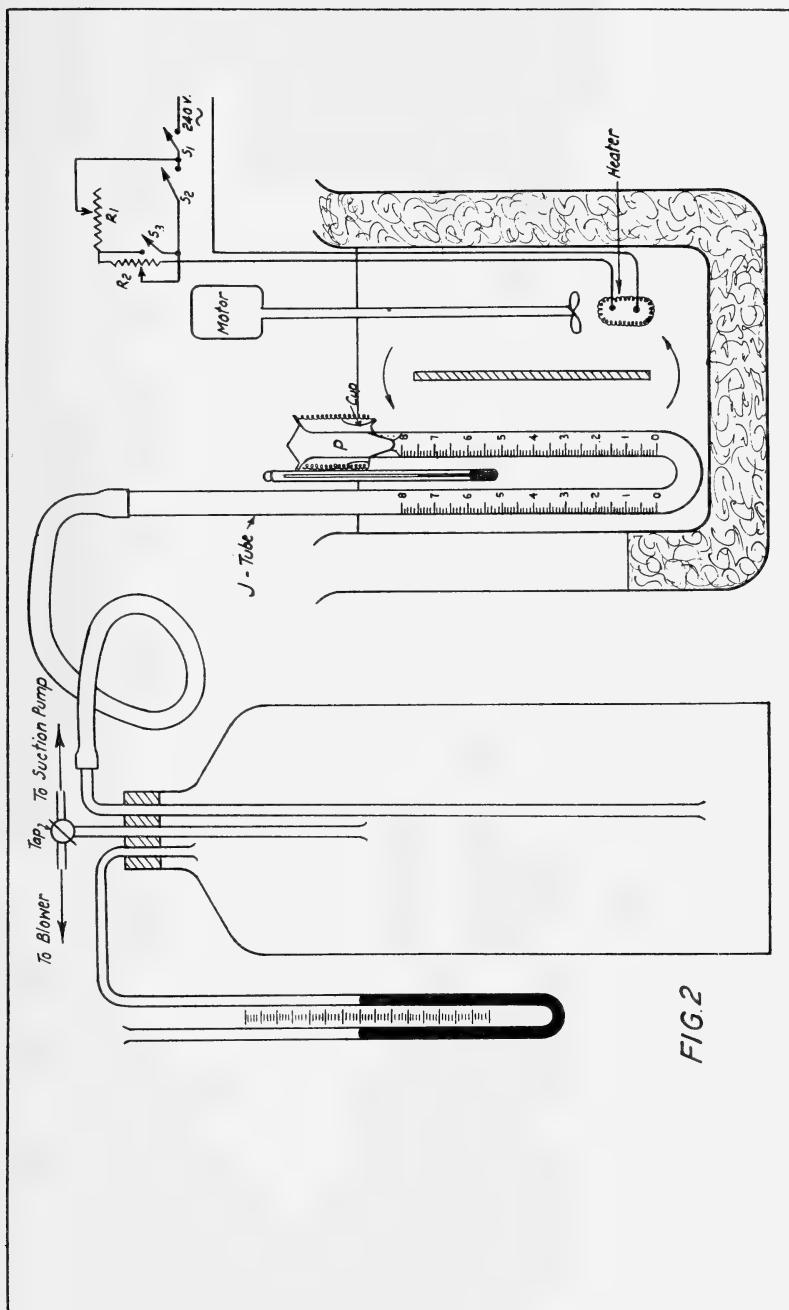


Fig. 2.—Boiling Point Apparatus.

shorter, including the stopper P, is about 14 cm. The stopper P is ground to a good fit in the socket at the top of the shorter limb and is surrounded by a cup

to retain a liquid seal. The stopper is held in place by spring ties. Both limbs are graduated in mm. from a datum line perpendicular to the axes of the limbs near the bend to a similar line just below the socket.

The heating bath consists of a large beaker containing paraffin B.P. or other high boiling transparent liquid. The beaker is well lagged except for the top and for an observation window in the side. In the beaker is supported a glass plate which touches the sides but whose upper and lower edges are about 2 cm. respectively below the liquid surface and above the bottom of the beaker. The motor-driven propeller causes the liquid to circulate rapidly as indicated by the arrows in Fig. 2.

The heater has a resistance of about 80 ohms. Switches  $S_1$ ,  $S_2$  and  $S_3$ , and the variable resistors  $R_1$  and  $R_2$ , enable the temperature of the bath to be raised or lowered rapidly or slowly at will.

The clean and dry J-tube, without the stopper, was clamped upright and into the shorter limb was poured enough of the nitric acid solution to reach a little more than half way up the millimetre scales. The tube was then placed in the heating bath so that the bath liquid reached about half-way up the side of the liquid seal cup when the propeller was in motion. The temperature of the bath was then rapidly raised by closing  $S_1$  and  $S_2$  until it was about  $3^\circ\text{C}$ . below the expected boiling point of the nitric acid solution.  $S_2$  was then opened and closed judiciously until the solution had boiled gently for a few seconds in order to out-gas it. The J-tube was then removed from the bath and switches  $S_1$  and  $S_2$  were opened.

The rubber tube from the Winchester air bottle was then slipped over the open end of the longer limb and slight air pressure was applied by manipulating the tap until the solution in the J-tube rose to partly fill the liquid seal cup; the meniscus in the longer limb was then near the bend in the tube. The stopper P was inserted in its socket and held in place by the spring ties. That portion of the solution which was trapped in the cup provided a liquid seal.

By this time the temperature of the bath had fallen well below the boiling point of the solution, and the J-tube was replaced in the bath, a plumb-line being used to ensure verticality of the limbs. Switches  $S_1$  and  $S_3$  were closed, and  $R_1$  was adjusted so that the bath temperature rose about  $\frac{1}{4}^\circ\text{C}$ . per minute;  $R_1$  was found to be about 170 ohms.

The barometer was then read and corrected for temperature and gravity. Using this corrected reading, the pressure in the Winchester air bottle was adjusted by manipulating the tap until the mercury manometer indicated that the total pressure in the bottle was  $760 \pm 0.5$  mm.

A short-stem thermometer, graduated in fifths of centigrade degrees, was clamped in the bath near the closed limb so that the graduation representing the expected boiling point was visible beneath the surface of the bath liquid through the inspection window.

As the temperature neared the boiling point of the solution, a vapour bubble formed beneath the stopper, and the solution was depressed in the shorter and raised in the longer limb.  $S_3$  was then opened and  $R_2$  adjusted so that the temperature fell about  $\frac{1}{4}^\circ\text{C}$ . per minute;  $R_2$  was then found to be about 50 ohms. By opening and closing  $S_3$  the temperature was adjusted until the menisci in the two limbs were at the same level. A final adjustment of the pressure in the bottle was made to ensure that it was 760 mm., and, if necessary, the bath temperature was altered slightly to compensate for this change in pressure. When the pressure in the bottle was within  $\frac{1}{2}$  mm. of 760 mm., and the levels of the solution in the two limbs differed by not more than 2 mm., the thermometer was read to the nearest  $0.1^\circ\text{C}$ . By manipulating  $S_3$  the temperature was

maintained nearly constant for five minutes, after which the pressure and temperature were again adjusted as above, and the temperature was again read. The J-tube was then removed from the bath, the rubber tube removed from the longer limb, and when the tube had cooled to ambient temperature, the solution was examined to see whether any uncondensed bubbles persisted beneath the stopper.

It was found that solutions containing more than 78 per cent. by weight of  $\text{HNO}_3$  decomposed and turned brown on heating as described above. The decomposition progressed while the temperature was maintained at a constant value, so that in order to keep the menisci of these solutions at the same level, it was necessary to increase the pressure in the air bottle. When the J-tube was subsequently cooled to room temperature, a large bubble of gas remained uncondensed beneath the stopper. The lowest concentration at which this decomposition was detected was at 77.4%  $\text{HNO}_3$  by weight, and the decomposition became increasingly apparent at higher concentrations.

*Standardization of the Thermometer.* The thermometer was tested by the Standards Laboratory, Sydney, over the range  $90^\circ\text{C}$ . to  $130^\circ\text{C}$ . for total immersion to an accuracy of  $\pm 0.2^\circ\text{C}$ ., and the reported corrections were applied to the readings.

*Preparation of Aqueous Solutions of Nitric Acid.* Solutions containing less than 70.2 per cent.  $\text{HNO}_3$  by weight were prepared by mixing weighed quantities of "Analar" concentrated nitric acid and distilled water. More concentrated solutions were prepared by mixing the "Analar" acid with a 98.5 per cent. nitric acid prepared as follows.

Equal volumes of "Analar" concentrated nitric acid and concentrated sulphuric acid were mixed and distilled at a pressure of about 10 cm. of mercury in an all-glass still. The resulting distillate was mixed with an equal volume of concentrated sulphuric acid and again distilled at about 10 cm. Hg.

The azeotropic solution was prepared by mixing weighed quantities of "Analar" acid and water to yield a 68 per cent. solution of  $\text{HNO}_3$ , and this was distilled at 760 mm. The first four-fifths of the distillate was rejected. The fact that the remainder of the distillate was truly the azeotropic mixture was assured by comparing its boiling point with the boiling points of mixtures of it with small quantities of concentrated acid and water respectively.

The concentrations of all solutions were determined by titration against sodium carbonate solution, using screened methyl orange indicator.

#### SUMMARY.

A method has been devised for the rapid determination of the boiling points of pure liquids and liquid mixtures which do not attack glass. The method obviates recourse to calculated corrections for emergent column and variations in atmospheric pressure, requires about 5 ml. of liquid, prevents sensible variations in composition of the liquid phase and avoids superheating. The method has been used to correct the list of boiling points of aqueous nitric acid appearing in the International Critical Tables. Solutions containing more than 78 per cent.  $\text{HNO}_3$  by weight are found to decompose at or before reaching their boiling points. The constant boiling solution of nitric acid in water at 760 mm. is found to contain  $67.5 \pm 0.5$  per cent. by weight  $\text{HNO}_3$  and to have a boiling point of  $120.6 \pm 0.2^\circ\text{C}$ . at 760 mm.

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## REDUCTION BY DISSOLVING METALS.

### PART VIII. SOME EFFECTS OF STRUCTURE ON THE COURSE OF REDUCTIVE FISSION.

By ARTHUR J. BIRCH, M.Sc., D.Phil.

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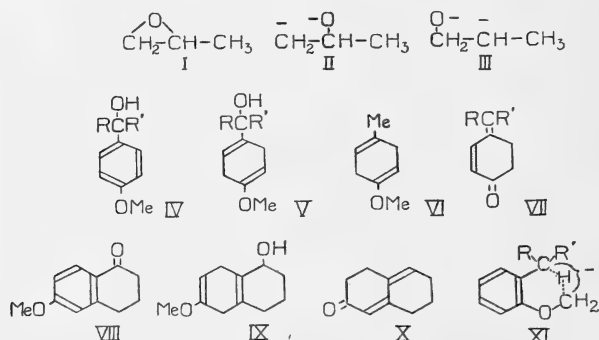
From an examination of the course of reductive fission by sodium-liquid ammonia solutions of diaryl ethers (Sowa *et al.*, 1937, 1938) and of aryl-alkyl ethers (Birch, 1947*a*) it has been concluded that the reactions proceed through transition states containing two anions:  $R-O-R'+2e \rightarrow (R^- + R'-O^-)$  or  $(R'^- + R-O^-)$ ; the chosen transition state being the one of lower energy. By far the greater part of the energy is required to produce the carbon anions  $R^-$  or  $R'^-$ , that needed for  $R-O^-$  or  $R'-O^-$  being negligible by comparison ( $ROH$ ,  $pK \approx 18$ , is a much stronger acid than  $RH$ ,  $pK \approx 37$ ). In practice it seems to be possible to neglect all other factors, e.g. differences in bond-strengths, and to compare the energies of the transition states on the basis of the energies of these carbon anions. The relations between structure and acidity (Birch, 1947*b*) lead to the conclusion that the greater the number of electron-repelling groups, such as alkyl, attached to a negatively charged carbon in a molecule, the greater will be its energy. Reduction should therefore proceed to give the least alkylated R-group as  $R^-$ .

This conclusion has been experimentally confirmed for aromatic systems (Birch, 1945, 1947*b*), which reduce because of resonance stabilisation of the anions, but has not been tested directly for saturated systems because they do not reduce. A confirmation of the theory in a similar case has now, however, been obtained by reducing 1:2-epoxypropane (I) to *isopropyl* alcohol. In this case the high ring-strain of the ethylene-oxide ring assists its reductive fission by contributing to the energy of the transition state (II). The same reduction can be carried out by sodium amalgam (Linnemann, 1866). That (II) should be formed rather than (III) can be predicted, because it contains  $CH_2^-$ , of lower energy than  $CH^-$ . The reaction cannot proceed by preliminary isomerisation to acetone, since acetone is largely unreduced under the conditions employed owing to the formation of its sodium salt.

The effect of a substituent in a benzene ring on the fission of aryl ethers (Sowa *et al.*, 1937, 1938; Birch, 1947*a*) is usually that to be expected from its known electronic character. The one outstanding exception so far examined is the methoxyl-group, whose influence depends on its position relative to the charged carbon atom formed in the process. In the *para*-position it shows the charge-destabilising effect to be expected from its normal electron-repelling character, but in the *ortho*-position it is charge-stabilising. In view of this unexpected dual behaviour, another reduction of a similar type, that of methoxy-phenylcarbinols, has been examined. The results confirm the orientation effects already observed: the *ortho*- and *meta*-methoxy-derivatives undergo reductive fission with loss of the hydroxyl-group, just as do the unsubstituted carbinols (Birch, 1945), e.g. 2- and 3-methoxyphenyl-carbinol give 2- and 3-*isopropyl*-anisole, but the *para*-methoxy-derivatives preponderantly retain the hydroxyl-group and reduce instead in the benzene ring. Small amounts of the fission

products are also obtained, but the only case where the amount is considerable is 4-methoxyphenylcarbinol (anisyl alcohol) (IV; R, R'=H), where it is clear from work already done (Birch, 1945) that the nuclear reduced compound (V; R, R'=H) can itself undergo reductive fission to the experimentally obtained 4-methyl-2:5-dihydroanisole (VI). The orientation of the two hydrogen atoms added to the benzene ring of the carbinol follows from the rule enunciated (Birch, 1944) and is confirmed by acid hydrolysis of the enol-ether group to a carbonyl. This hydrolysis is accompanied by dehydration to give the interesting diene-ketones (VII; R, R'=H or Me).

Anisyl alcohol produces a mixture of 4-methoxy-2:5-dihydrophenylcarbinol (V; R=R'=H), hydrolysed by acid to 4-methylenecyclohex-2-enone (VII; R=R'=H), and 4-methyl-2:5-dihydroanisole (VI). 4-Methoxyphenylmethylcarbinol (IV; R=H, R'=Me) gives chiefly 4-methoxy-2:5-dihydrophenylmethylcarbinol (V; R=H, R'=Me) hydrolysed to 4-ethylidenecyclohex-2-enone (VII; R=H, R'=Me),  $\lambda_{\max}$  2,850 Å. Similarly, 4-methoxyphenyldimethylcarbinol (IV; R=R'=Me) gives 4-methoxy-2:5-dihydrophenyldimethylcarbinol, hydrolysed to 4-isopropylidenecyclohex-2-enone (VII; R=R'=Me). A particularly interesting case is the reduction of 1-keto-6-methoxy-1:2:3:4-tetrahydronaphthalene (VIII) to give 1-hydroxy-6-methoxy-1:2:3:4:5:8-hexahydronaphthalene (IX), hydrolysed by acid to 3-keto-1:2:3:5:6:7-hexahydronaphthalene (X). The light absorption of the last compound at  $\lambda_{\max}$  2,900 Å. is in accord with its structure as a conjugated diene-ketone.



In all these cases, the transition state of reductive fission, e.g.  $(4\text{-MeOC}_6\text{H}_4\text{CRR}' + \text{OH}^-)$  evidently requires so high an energy because of the influence of the *para*-methoxyl that the benzene ring is reduced for preference. That normal reductive fission occurs with the *meta*-methoxy compound is not astonishing, since the effect of a group in a *meta*-position is small, but the behaviour of the *ortho*-compound requires some explanation. One possible reason is that the methoxyl-group has a dual electronic character: an electron-attracting character due to the higher nuclear charge on the oxygen, and an electron-repelling character due to the unshared electrons of the oxygen atom. It is the latter which is usually more effective, especially if the group is attached to a polarisable system. There seems no reason, however, to expect one effect to operate for an *ortho*-group and the other for a *para*-group. A more likely explanation is that the *ortho*-negative charge is stabilised by cyclic hyperconjugation, which partly transfers it to the carbon of the methoxyl-group (XI). If this explanation is correct, no stabilisation should be observed with *tert*-butyl ethers lacking the necessary hydrogen atom. It is hoped to test this experimentally. It may be of significance that anisoles and 2:5-dihydroanisoles invariably metallate in the *ortho*-position, i.e. the *ortho*-anions are the most readily formed.

The ease of reductive fission is also altered if the energy of formation of the transition state is altered in other ways. If a negative charge is placed by salt formation on the oxygen atom of an allyl or benzyl alcohol, the fission is prevented. For example, it was shown (Birch, 1945) that  $\text{PhCH}=\text{CHC}(\text{CH}_3)_2\text{OH}$  is converted by sodium and alcohol in liquid ammonia into two products:  $\text{PhCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$  by reduction of the double bond, and  $\text{PhCH}_2\text{CH}=\text{C}(\text{CH}_3)_2$  by reductive fission. However, the sole product from the sodium salt  $\text{PhCH}=\text{CHC}(\text{CH}_3)_2\text{ONa}$  is the dihydro-alcohol, the oxygen remaining in the molecule.

If the oxygen of an ether or alcohol is replaced by nitrogen then reductive fission of the amine is usually impossible; e.g. benzylamines, unlike benzyl ethers or alcohols, are usually unaffected by sodium in liquid ammonia. This is due to the higher energy of formation of the nitrogen anion compared with the oxygen anion: amines are very weak acids compared with alcohols. However, if the nitrogen is charged positively by quaternary salt formation it can be reductively eliminated, not as an anion, but as an electrically neutral amine. The energy of the transition state is thus greatly lowered. Although dimethylaniline gives mainly the 2:5-dihydro-derivative (Birch, 1946) phenyltrimethylammonium iodide gives benzene, and benzyltrimethylammonium iodide gives toluene, the nitrogen appearing as trimethylamine. The reaction is a variant of the well-known Emde reaction using sodium-amalgam (e.g. Emde and Kull, 1934), but is much more powerful. For example, the Emde method reduces phenyltrimethylammonium salts only with great difficulty (e.g. Emde, 1909). The sodium-ammonia method may prove a useful tool in alkaloid degradation (Clayson, 1949).

#### EXPERIMENTAL.

##### *Reduction of 1:2-epoxypropane (I).*

1:2-Epoxypropane (7 g.) was added to a solution of sodium (6 g.) in ammonia (200 cc.) and left until the ammonia had evaporated. The residue was cautiously decomposed with a little ice, extracted with ether ( $2 \times 5$  cc.), the solution dried with potassium carbonate, and the ether removed through a small but efficient column. The residue (3.2 g.) distilled completely at  $80\text{--}82^\circ$ , and gave the 3:5-dinitrobenzoate of isopropanol as cream needles m.p.  $108\text{--}109^\circ$ , undepressed by an authentic specimen.

##### *Reduction of Some Methoxyphenylcarbinols.*

With the exception of 4-methoxyphenylcarbinol, which was purchased, the carbinols were made by the Grignard reaction between methylmagnesium iodide and the appropriate aldehyde or ketone. The trouble reported in the literature in the preparation of 4-methoxyphenyldimethylcarbinol, due to dehydration, was not encountered if the Grignard product was worked up without the use of acid, and the ether solution well washed with water and dried over potassium carbonate.

Reduction was accomplished by dissolving the carbinol (10 g.) and ethanol (20 cc.) in ammonia (150 cc.) and adding sodium (2.2 mol.) in small pieces with mechanical stirring. In later experiments with the object of preparing the 4-methoxy-2:5-dihydrophenylmethyl- and dimethylcarbinol, the amount of sodium was raised to 5 mol. to ensure complete reduction of the ring. The reduction products were worked up by the addition of water (100 cc.), extraction with ether ( $3 \times 25$  cc.) and distillation. The products of reductive fission were redistilled over sodium to remove any traces of carbinol.

(a) 2-Methoxyphenylmethylcarbinol, b.p.  $130^\circ/16$  mm. (Klages, 1903) gave 2-ethylanisole, b.p.  $80^\circ/14$  mm. (7 g.) (found: C, 79.5; H, 9.0%. Calculated for  $\text{C}_9\text{H}_{12}\text{O}$ : C, 79.4; H, 8.8%).

The product, as might be expected (Birch, 1944), contained traces of ethyldihydroanisole, because the action of 2:4-dinitrophenylhydrazine in 2 N hydrochloric acid and steam-distillation,

left a residue which was separated by crystallisation from alcohol into two substances. The more insoluble crystallised from ethyl acetate in dark red plates, m.p. 225°, and is probably *2-ethylcyclohex-2-enone 2:4-dinitrophenylhydrazone* (found: C, 55.0; H, 5.1%.  $C_{14}H_{16}O_4N_4$  requires C, 55.2; H, 5.2%); the more soluble formed orange-red needles from ethanol, m.p. 118–119°, and is probably *2-ethylcyclohex-5-enone 2:4-dinitrophenylhydrazone* (found: C, 55.2; H, 5.0%.  $C_{14}H_{16}O_4N_4$  requires C, 55.2; H, 5.2%) (cf. the reduction of 2-methylanisole, Birch, 1944).

(b) 2-Methoxyphenyldimethylcarbinol (Béhal and Tiffeneau, 1908) gave 2-isopropylanisole (7.4 g.) b.p. 93–95°/18 mm. (found: C, 79.8; H, 9.5%. Calculated for  $C_{10}H_{14}O$ : C, 80.0; H, 9.3%). 3-Methoxyphenyldimethylcarbinol (Béhal and Tiffeneau, 1908) reduced to 3-isopropylanisole, b.p. 93–95°/16 mm. (found: C, 81.1; H, 9.5%. Calculated for  $C_{10}H_{14}O$ : C, 80.0; H, 9.3%). This contained a trace of the 2:5-dihydro-derivative, since the action of 2:4-dinitrophenylhydrazine as above gave 3-isopropylcyclohex-2-enone 2:4-dinitrophenylhydrazone, bright red prisms from ethyl acetate, m.p. 155° (found: C, 54.6; H, 5.6%.  $C_{15}H_{18}O_4N_4$  requires C, 56.6; H, 5.7%). With none of these compounds was there more than a trace of higher-boiling material from the reduction.

(c) Anisyl alcohol (with 3.0 mol. of sodium) gave a mixture of a product (A) (3.1 g.) b.p. 80°/20 mm., and (B) (4.2 g.) b.p. 135°/12 mm. Fraction (A) consisted principally of 4-methyl-2:5-dihydroanisole, because the action of dilute acid (Birch, 1944) gave 4-methylcyclohex-3-enone, semicarbazone m.p. 188°, 2:4-dinitrophenylhydrazone m.p. 122°. Fraction (B) consisted principally of 4-methoxy-2:5-dihydrophenylcarbinol (found: C, 68.9; H, 8.2%.  $C_8H_{12}O_2$  requires C, 68.6; H, 8.6%) (cf. Birch, 1945). On warming on the steam-bath with 1 N sulphuric acid for ten minutes, it first dissolved and then an oil separated. This was taken up in ether, and distilled in a stream of nitrogen, b.p. 75–77°/12 mm. It was very unstable, and rapidly polymerised to a clear rubbery solid. It was not analysed for this reason, but gave rise to the derivatives expected for 4-methylenecyclohex-2-enone: the semicarbazone crystallised as cream needles from alcohol m.p. 192° (decomp.) (found: C, 57.9; H, 6.7%.  $C_8H_{11}ON_3$  requires C, 58.2; H, 6.7%) (if slowly heated the derivative polymerised to a pale yellow resin without melting); and 2:4-dinitrophenylhydrazone as large flat red needles from ethyl acetate, m.p. 160–161° (found: C, 53.8; H, 4.2%.  $C_{13}H_{12}O_4N_4$  requires C, 54.2; H, 4.2%).

(d) 4-Methoxyphenylmethylcarbinol (Klages, 1903) reduced to give mainly 4-methoxy-2:5-dihydrophenylmethylcarbinol (6.5 g.) b.p. 130°/14 mm. (found: C, 68.9; H, 9.3%.  $C_9H_{14}O_2$  requires C, 70.1; H, 9.1%) hydrolysed by hot 5% sulphuric acid to 4-ethylidenecyclohex-2-enone b.p. 100–103°/14 mm.  $\lambda_{\max}$  2,850,  $\epsilon_{\max}^{\text{mol}}$  12,800 (found: C, 78.9; H, 8.9%.  $C_8H_{10}O$  requires C, 78.7; H, 8.2%); 2:4-dinitrophenylhydrazone, dark red plates from ethylacetate m.p. 164° (found: C, 55.1; H, 4.8%.  $C_{14}H_{14}O_4N_4$  requires C, 55.6; H, 4.6%); semicarbazone, cream-coloured needles from ethanol m.p. 192° (found: C, 60.2; H, 7.5%.  $C_9H_{13}ON_3$  requires C, 60.3; H, 7.3%).

(e) 4-Methoxyphenyldimethylcarbinol, b.p. 130°/14 mm. (Skraup and Freundlich, 1922) gave 4-methoxy-2:5-dihydrophenyldimethylcarbinol (8 g.) b.p. 128–130°/12 mm. (found: C, 70.9; H, 9.0%.  $C_{10}H_{16}O_2$  requires C, 71.4; H, 9.5%). Acid hydrolysis gave 4-isopropylidenecyclohex-2-enone (5.2 g.) b.p. 117–119°/12 mm. (found: C, 78.9; H, 8.7%.  $C_9H_{12}O$  requires C, 79.4; H, 8.8%); 2:4-dinitrophenylhydrazone m.p. 157° (found: C, 56.7; H, 5.1%.  $C_{15}H_{16}O_4N_4$  requires C, 57.0; H, 5.0%); semicarbazone, cream-coloured needles from ethanol, m.p. 206–207° (found: C, 61.9; H, 7.8%.  $C_{10}H_{15}ON_3$  requires C, 62.2; H, 7.8%).

(f) Reduction of 1-keto-6-methoxy-1:2:3:4-tetrahydronaphthalene (Stork, 1947) (7 g.) was carried out by dissolving it in warm ethanol (25 cc.), and adding the solution with vigorous stirring to ammonia (250 cc.), followed by addition of sodium (7 g.) in small pieces. Working up and distillation of the product gave two fractions: (A) b.p. up to 100°/0.4 mm. (condenser in a freezing-mixture) and (B) b.p. 100–130°/0.4 mm. Fraction (A) was heated on the steam-bath with 1 N sulphuric acid for fifteen minutes, and the oil treated with aqueous-alcoholic semicarbazide acetate. The solid so obtained was the semicarbazone of 3-keto-1:2:3:5:6:7:8:9-octahydronaphthalene, m.p. 216°, undepressed by an authentic specimen. This is the product to be expected from 6-methoxy-1:2:3:4:5:8-hexahydronaphthalene. The



residual oil from the treatment was redistilled over sodium, (0.3 g.) b.p. 193–197°, and is probably a mixture of hexahydronaphthalenes (found: C, 89.2; H, 10.4%. Calculated for  $C_{10}H_{14}$ : C, 89.6; H, 10.4%.) Fraction (B) was redistilled, and the main fraction (3.4 g.) had b.p. 124–126°/0.4 mm. It solidified, and was crystallised from light petroleum (b.p. 40–60°) as massive prisms, m.p. 76–77° (2.9 g.). It analysed for 1-hydroxy-6-methoxy-1:2:3:4:5:8-hexahydronaphthalene (found: C, 73.6; H, 9.0%.  $C_{11}H_{16}O_2$  requires C, 73.3; H, 8.9%.) After refluxing with 1 N sulphuric acid for thirty minutes the pleasant-smelling 3-keto-1:2:3:5:6:7-hexahydronaphthalene was distilled, b.p. 141°/12 mm. (found: C, 80.8; H, 8.3%.  $C_{10}H_{12}O$  requires C, 81.0; H, 8.1%.) The light absorption  $\lambda_{\max}$  2,900 Å,  $\epsilon_{\max}^{mol}$  13,400, is in agreement with its formulation as a conjugated doubly-unsaturated ketone. The semicarbazone crystallised in cream-coloured prisms from ethanol, m.p. 210–211° (found: C, 64.4; H, 7.2%.  $C_{11}H_{15}ON_3$  requires C, 64.4; H, 7.3%.)

#### *Reduction of Quaternary Ammonium Salts.*

Phenyltrimethylammonium iodide (20 g.) and alcohol (15 g.) in ammonia (100 cc.) underwent a vigorous reaction with sodium (4 g.). Addition of water (100 cc.) and separation of the oil (centrifuge) gave benzene (3 g.) b.p. 80°,  $n_D^{19}$  1.4900, 1:3-dinitro-derivative m.p. 88°, undepressed by an authentic specimen. Benzyltrimethylammonium iodide similarly gave toluene, b.p. 110°, converted to 2:4-dinitrotoluene m.p. 70°, undepressed by an authentic specimen. Benzylamine or benzyldibutylamine under the same conditions gave no hydrocarbon product.

#### *Reduction of 3-hydroxy-1-phenyl-3-methylbut-1-ene.*

The carbinol (8 g.) was reacted in ammonia (100 cc.) with finely powdered sodium amide (2 g.) and then sodium (2 g.) added. The blue colour disappeared and was replaced by a brownish-red one. Working up by addition of water, ether extraction and distillation gave 3-hydroxy-1-phenyl-3-methylbutane (7.3 g.), b.p. 130°/18 mm. (found: C, 80.5; H, 9.7%. Calculated for  $C_{11}H_{16}O$ : C, 80.4; H, 9.75%.) It gave the phenylurethane m.p. 140°, undepressed by an authentic specimen.

#### SUMMARY.

The following reductions have been carried out by the action of sodium in liquid ammonia: 1:2-epoxypropane to isopropyl alcohol; several 2- and 3-methoxyphenylcarbinols to the corresponding ethylanisoles, and some 4-methoxyphenylcarbinols preponderantly to 2:5-dihydro-derivatives, hydrolysed and dehydrated by the action of acid to 4-alkylidenecyclohex-2-enones. Phenyl- and benzyltrimethylammonium iodide give benzene and toluene respectively; the sodium salt of 3-hydroxy-1-phenyl-3-methylbut-1-ene gives solely 3-hydroxy-1-phenyl-3-methylbutane. These results are discussed in relation to the theory that such reductive fissions involve the formation of transition states containing two anions.

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# PEBBLES FROM THE UPPER HUNTER RIVER VALLEY, N.S.W.

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## INTRODUCTION.

This paper presents the results of an examination of samples of pebbles from Triassic (Lower Narrabeen) conglomerates, from Permian (Upper Coal Measures, Muree Beds, Branxton Beds, Greta Coal Measures) conglomerates, and from gravels of certain river terrace soils. The samples were collected during a soil survey from a number of localities between Denman and Murrurundi (localities are given in Table 1).

The geology of the area has been described by David (1907), Browne (1924), Raggatt (1929; 1938) and Dulhunty (1939), and the physiography by Browne (1924) and Sussmilch (1940). The present Upper Hunter River and its tributaries are flowing in a wide mature valley in which they are slightly entrenched owing to uplift. The valley has a floor of Permian sediments; it is bounded on the west by an escarpment of Triassic conglomerates overlain in places by a thin bed of Jurassic sediments, and capped by Tertiary basalt; the eastern side of the valley is largely in Carboniferous rocks (Kuttung series) and Permian sediments. In Tertiary and post-Tertiary times the Hunter and its tributaries have deposited alluvial flats and river gravels. Remnants of Tertiary basalts occur in parts of the valley.

The original Upper Hunter after flowing out of the resistant Carboniferous rocks followed the strike of the soft westerly dipping Permian sediments and of the Wingen fault. The river enlarged its valley on the western side by the removal, due to sapping, of the hard resistant Triassic conglomerates overlying the Permian rocks (Browne, 1924, 139). Raggatt (1938) indicated that the original eastern boundary of Triassic deposition was not far east of Muswellbrook. If this is so, then the resistant material derived from the Triassic conglomerate would probably remain, in part at least, in the river valley, particularly near its western side. Rock wastage at the present time adds material to the valley sediments. The old valley floor remains as at least two river terraces, the higher at about 150 feet above the present river level (see 1 : 63, 360 Military Maps, sheets 368 and 377, zone 8). The river terraces often contain gravel which may (a) have been transported from different sources during river development; (b) have been derived by the weathering *in situ* of Permian conglomerate beds; or (c) be derived wholly or in part from the Triassic conglomerates.

In order to characterise the pebbles derived from various sources, samples were collected from the localities shown in Table 1. Samples G3-G12, G14, G15, G18 were collected from locations thought to represent the 150-foot terrace level. Of the remaining samples given in Table I, G1 and G2 are representative of the Upper Coal Measure conglomerates; G16, the Muree conglomerate; G17, the Greta Coal Measure conglomerate. G13 was taken from a soil apparently developed on the Branxton Beds (details of these beds are given by Raggatt, 1929 and 1938).

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\* Division of Soils, Commonwealth Scientific and Industrial Research Organization.

TABLE 1.  
Description and Locality of Samples Examined.

Sample No.	Locality.	Description.
N1	West of Temple Court, near Mur-rurundi, Co. Brisbane, Pa. Mur-rurundi, Por. 27.	Lower Narrabeen conglomerate, top of cliff, 120 ft. above ground-level.
N2	" " " "	Lower Narrabeen conglomerate, 50 ft. above ground-level.
N3	" " " "	Lower Narrabeen conglomerate, 3 ft. above ground-level.
N4	South of Mt. Murella, Co. Brisbane, Pa. Tingaroo, Por. 217.	Lower Narrabeen conglomerate, base of cliffs.
N5	West of Wingen, Co. Brisbane, Pa. Wingen, Por. 168.	Lower Narrabeen conglomerate, base of cliffs.
N6	Bunnan Rd., W. of Scone, Co. Brisbane, Pa. Manbus, Por. 102.	Lower Narrabeen conglomerate, base of cliffs.
N7	" " " "	Lower Narrabeen sandstone, base of cliffs.
N8	West of Dartbrook Lone, Co. Brisbane, Pa. Halscott, Por. 138.	Lower Narrabeen conglomerate, top of cliffs.
N9	" " " "	Lower Narrabeen sandstone, top of cliffs.
N10	" " " "	Lower Narrabeen sandstone, 80 ft. below top of cliffs.
N11	" " " "	Lower Narrabeen coarse sandstone, base of Triassic outcrop.
N12	8 miles N.E. of Sandy Hollow, Co. Brisbane, Pa. Yarraman, Por. 43.	Lower Narrabeen conglomerate, base of cliffs.
N13	Denman-Merriwa Rd., Co. Brisbane, Pa. Denman, Por. 22.	Lower Narrabeen conglomerate, top of cliffs.
N14	" " " "	Lower Narrabeen conglomerate, half-way up cliffs.
N15	" " " "	Lower Narrabeen conglomerate, base of cliffs.
G1	S. of Muswellbrook on Hunter River, Co. Durham, Pa. Vaux, Por. 86.	Gravel from Upper Coal Measure conglomerate.
G2	S. of Kyuga, Co. Brisbane, Pa. Ellis, Por. 4.	Gravel from Upper Coal Measure conglomerate.
G3	W. of Muswellbrook, Co. Brisbane, Pa. Clanricard, Por. 9.	Gravel from soil developed on Upper Coal Measures; river terrace.
G4	Kingdon Ponds, Co. Brisbane, Pa. Strathearn, Por. 47.	Gravel from soil developed on Upper Coal Measures; river terrace.
G5	W. of junction of Dart Brook and Hunter R., Co. Brisbane, Pa. Strathearn, Por. 39.	Gravel from soil developed on Upper Coal Measures conglomerate.
G6	S.W. of Muswellbrook, Co. Brisbane, Pa. Clanricard, Por. 5.	Gravel from soil developed on Upper Coal Measures. ? River terrace.
G7	S.W. of Muswellbrook, Co. Brisbane, Pa. Clanricard, Por. 3.	" " " "
G8	Scone, Co. Brisbane, Pa. Scone, Por. 10.	Gravel from soil developed on Upper Coal Measures; river terrace.
G9	2 miles S. Scone, Co. Brisbane, Pa. Scone, Por. 9.	Gravel from soil developed on Upper Coal Measures. ? River terrace.
G10	Near junction of Pages and Hunter R., Co. Durham, Pa. Russell, Por. 347.	" " " "
G11	Hunter R., S. Muswellbrook, Co. Durham, Pa. Vaux, Por. 1.	Gravel from soil developed on Upper Coal Measures; river terrace.
G12	Dart Brook, Co. Durham, Pa. Strathearn, Por. 35.	Gravel from soil developed on Upper Coal Measures; probable Triassic contamination; ? river terrace or colluvial slope.
G13	St. Helier's Brook, Co. Durham, Pa. Russell, Por. 8.	Gravel from soil developed on Branxton Beds.

TABLE 1.—*Continued.*  
*Description and Locality of Samples Examined.*—Continued.

Sample No.	Locality.	Description.
G14	Muswellbrook, Co. Durham, Pa. Rowan, Por. 139.	Gravel from soil developed on Branxton Beds; river terrace.
G15	Muswellbrook, Co. Durham, Pa. Rowan, Por. 2.	Gravel from soil developed on Branxton Beds; ? river terrace.
G16	N.E. Muswellbrook, Co. Durham, Pa. Rowan, Por. 57.	Gravel from soil developed on Muree Beds.
G17	1 mile E. Muswellbrook, Co. Durham, Pa. Rowan, Por. 181.	Conglomerate from the Greta Coal Measures.
G18	7 miles S. Muswellbrook, Co. Durham, Pa. Vaux, Por. 3.	Gravel from soil developed on Upper Coal Measures; river terrace.

The soils from which the pebbles were collected fall into two main groups which include all the gravelly soils of the area. These are:

(1) Soils related to the Red-brown Earths. This group of soils generally has a surface  $A_1$  horizon of dark brown to dark grey-brown loam or clay-loam over a  $B_1$  illuvial horizon of brown clay. Lime is sporadic and may or may not show an accumulation in the  $B_2$  horizon. The deep subsoil (BC horizon) becomes gradually yellowish. G3–9, G11–15 and G17–18 all belong to this group, with some variation in the profile morphology, chiefly as regards colour of the  $B_1$  horizon, which varies from red-brown in G9 and G12 to dark brown in G3, 7, 14, 17, 18, and greyish yellow in G5. Most of the terrace soils fall into this group.

(2) Soils related to the Black Earths. These generally have a well structured dark brown clay surface which becomes browner with depth; a zone of lime accumulation occurs in the BC horizon. G10 belongs to this group.

G16 was taken from the surface of a podsollic soil developed on the Muree Beds. The soil description has no significance because it is not a type represented on the river terraces.

#### EXAMINATION OF SAMPLES.

(a) *Fundamental Properties.* Sedimentary materials have a number of fundamental properties which can be used to provide data for descriptive purposes. Composition, size, shape and roundness of the pebble samples were examined by means of lithology counts, mechanical analysis (giving the variation in size of the pebbles and the amount of sorting), description of the roundness and sphericity.

*Lithological Composition.* Lithology counts of the kinds of rock in the pebbles contained in a conglomerate, river gravel or other material give precision to descriptions of these sediments, and if a sufficiently large number of samples is collected the results can be treated statistically. Conglomerates naturally vary somewhat in lithology from place to place even if belonging to the same bed. The diagnostic value of lithology counts is indicated in recently published papers by Allen (1949) and Plumley (1948). Materials which have been transported considerable distances will have lost their softer and more easily weatherable pebbles and will consist mainly of the most resistant types of rock such as quartz and chalcedony.

*Mechanical Composition.* One of the fundamental properties of sedimentary fragments is size, and the size distribution of the constituents is often

characteristic, e.g. in dune sands. The size is important in connexion with the action of the transporting agent. When all the fragments in a sediment are found within one or two grade-sizes the sediment is considered to be well sorted.

In describing conglomerates the proportion of pebbles to matrix is of interest as it is considered unlikely that a very fine-grained clayey matrix such as that present in the Lower Narrabeen conglomerate could be deposited at the same time as large pebbles, a decrease in stream or current velocity being indicated (Plumley, 1948, 544).

*Roundness and Sphericity of Pebbles.* Roundness is a measure of the curvature of the corners and edges of fragments, and is expressed as a ratio to the average curvature of the fragment as a whole, independent of its form. This is based on the curvature of surfaces as discussed by Thomson and Tait (1879, 101). Roundness indicates wear, probably by transport, but is difficult to interpret as different sized pieces of the same material in the same bed may, and generally do, show different degrees of roundness. Allen (1949, 310) states that the estimation of "roundness" is not yet satisfactorily measured for statistical treatment.

The shape is important in the selective transportation of fragments. Shape may be a useful feature when comparing pebbles believed to be from the same source and to have undergone similar conditions of transport. The final shape which rock materials will assume on continued wear has not yet been determined with any degree of certainty (Rayleigh, 1942; 1944). It is probably only homogeneous material, fine and even grained, non-laminated, or from thick even beds among sedimentary rocks which will tend to assume a spherical shape. Observation of pebbles in a number of situations indicates that lamination, bedding and jointing are important original factors.

(b) Method of Examination.

#### *Preliminary Treatment.*

(i) *Conglomerates.* The field samples were carefully crushed in an iron mortar to free the pebbles from the matrix without breaking them. Some samples had a matrix harder than the pebbles and no unbroken pebbles could be obtained. The crushed material was quartered down until a representative sample of 2,000 to 3,000 gm. was obtained. All examinations were made on these samples.

(ii) *Gravelly Soils.* The pebbles were separated by washing out the soil and representative samples obtained as in (i).

*Mechanical Analysis.* The size composition of the pebbles in all samples was obtained by sieving through a set of sieves with square mesh openings of 1,  $\frac{1}{2}$ ,  $\frac{1}{4}$  and  $\frac{1}{8}$  inch diameter (approximately 25, 12.5, 6.25 and 3 mm. respectively). These sizes fall within the Wentworth (1922) pebble grade, 64—4 mm., with the exception of the smallest. It was not possible to obtain sieves giving the Wentworth scale which would have been desirable for comparison with pebbles described from other localities. The results of the mechanical analyses are given in Tables 3, 6 and 9. (All tables appear at the end of this paper.)

*Lithology Counts.* The rock types were identified in the  $-1 + \frac{1}{2}$  in. grade of the pebble samples from soils and Permian conglomerates, and in the  $-\frac{1}{2} + \frac{1}{4}$  in. grade of the Lower Narrabeen conglomerates. The total number of pebbles present in each of these grades was identified, and amounted to between 100 and 150 in the soil pebble samples, and 50 to 100 in the conglomerates (see Tables 2, 5 and 8).

*Determination of Roundness of Pebbles.* The roundness of jasper, chalcedony and chert pebbles was determined in samples of the soils and Permian conglomerates,  $-1 + \frac{1}{2}$  in. grade with the exception of three samples, Nos. G1,

TABLE 2.

*Lithology of Pebbles in the  $-\frac{1}{2}+\frac{1}{4}$  inch Grade, Lower Narrabeen Conglomerate.*  
(Percentage by Number.)

Sample No. . . . .	N6	N8	N9	N10	N11	N12	N14	N15
Rock types :								
Quartz . . . . .	3	6	15	—	3	—	—	—
Jasper . . . . .	10	6	8	23	10	15	4	—
Chert and chalcedony . . . . .	46	63	38	38	41	49	46	65
Sedimentary* . . . . .	36	22	38	38	45	20	22	34
Quartzite . . . . .	—	—	—	—	—	—	1	—
Acid igneous† . . . . .	—	1	—	—	—	15	21	—
Tuff . . . . .	3	—	—	—	—	—	2	—

\* Sedimentary rocks include claystone, sandstone (fine and coarser), indurated shale.

† Acid igneous rocks include rhyolite, felsite and allied types.

TABLE 3.

*Size Composition of Pebbles in the Lower Narrabeen Conglomerate.*  
(Grade units are in inches ; Percentage by weight.)

Grade.	$-1+\frac{1}{2}$ .	$-\frac{1}{2}+\frac{1}{4}$ .	$-\frac{1}{4}+\frac{1}{8}$ .	$-\frac{1}{8}$ Coarse Sand + Matrix.
Sample No.—	%	%	%	%
N6 . . . . .	2.0	4.7	4.0	89.3
N7 . . . . .	—	—	2.5	97.5
N8 . . . . .	15.6	22.0	27.0	36.4
N9 . . . . .	3.4	3.0	0.5	93.1
N10 . . . . .	—	8.0	9.3	82.7
N12 . . . . .	21.0	33.0	18.0	28.0
N14 . . . . .	17.0	43.0	18.0	22.0
N15 . . . . .	15.0	31.0	23.0	31.0

TABLE 4.

*Roundness and Sphericity of Pebbles from the Lower Narrabeen Conglomerate*  
( $-\frac{1}{2}+\frac{1}{4}$  inch Grade).

Sample No.—	Mean Roundness.	Mean Sphericity.	Zingg Classification.*
N6 . . . . .	0.42	0.75	11
N8 . . . . .	0.54	0.78	1
N9 . . . . .	0.27	0.75	11
N10 . . . . .	0.40	0.76	11
N11 . . . . .	0.46	0.71	1
N12 . . . . .	0.50	0.74	11
N14† . . . . .	0.52	0.75	11
N15 . . . . .	0.56	0.73	11

\* The shape of pebbles in Zingg's classification is : Class I, discs ; Class II, spherical ; Class III, blades ; Class IV, rod-like.

† Chalcedony pebbles only.

G2 and G10, in which the acid igneous rock pebbles were used because of the low content of jasper and chalcedony. In the Lower Narrabeen conglomerates all the pebbles in the  $-\frac{1}{2} + \frac{1}{4}$  in. grade were used. The roundness was determined visually by comparison with Krumbein's (1941) pebble images (see Tables 4, 7 and 10).

*Shape of Pebbles.* The shape was determined by Krumbein's intercept method (1941) which is based on a triaxial ellipsoid as the reference solid to which a pebble is compared (this implies that a sphere is the final shape towards which a pebble is progressing through abrasion, a fact which is not yet proved). It is therefore necessary to define the three diameters of a pebble as mutually perpendicular intercepts. The three diameters measured are designated as *a* (long), *b* (intermediate) and *c* (short). After the measurements have been made the ratios *b/a* and *c/b* are obtained and these are laid off on the axes of Krumbein's chart from which the sphericity figure is obtained. The Zingg (1935) pebble shape, based on the ratio of *b/a* to *c/b* is also given in Tables 4, 7 and 10. The measurements were made with a gauge similar to that illustrated by Krumbein (1941). An average of thirty randomly chosen pebbles of jasper and chalcedony from the  $-1 + \frac{1}{2}$  inch grade of soils and Permian conglomerates was measured to give the figures in Tables 7 and 10. Similar representative pebbles from the Lower Narrabeen conglomerates were used for the figures in Table 4.

#### DISCUSSION OF RESULTS.

##### Lower Narrabeen Conglomerate.

The Triassic rocks of the district were first described by Carne (1906, 55), who noted the "chalcedonic and jasperoid constituents of the pebbles and boulders. Red and green are the predominant colours, whilst ordinary white quartz pebbles are rarer and smaller". He considered that the pebbles were derived from altered Carboniferous and Devonian sediments to the north. On the other hand the Permian conglomerates are of quartz pebble character which distinguishes them from the Triassic conglomerates (*ibid.*, 53). Raggatt (1938), however, found difficulty in distinguishing the Permian from the Triassic conglomerates on lithological grounds alone. Dulhunty (1939) noted the presence of an upper portion about 250 ft. thick of homogenous medium-grained sandstone and a lower, 400 ft. thick, of conglomerate "being made up of coarse-grained sandstone packed with small rounded pebbles, mainly white quartz with a limited amount of red and black jasper" (*ibid.*, 32).

The Lower Narrabeen conglomerate was sampled at the base, middle and top of the lower portion of these Triassic beds. When examined in hand specimen, the basal Narrabeen conglomerate between Murrurundi and Denman is seen to be massive with a fine-grained, firmly cemented, clayey matrix which encloses pebbles of chalcedony, jasper, clayey sandstone and quartz, varying in size from about one-eighth inch to over one inch in diameter, the majority being about one-half inch in diameter. The matrix is very seldom sandy, and may be so hard that it is impossible to remove pebbles without breaking them. From this it may vary to softer material and finally to sandy lenses with few pebbles. On superficial examination the bed appears to be fairly uniform both laterally and vertically, but the mechanical analyses indicate that this is not so. On weathering the softer pebbles and matrix are removed first, leaving jasper and chalcedony prominent. The lithological composition is given in Table 2, which shows that chert and chalcedony are the most abundant constituents, followed by various sedimentary rocks. Quartz is not abundant except in N9; only two samples, N12 and N14, contain appreciable amounts of acid igneous rock pebbles. Jasper is always more plentiful than black chert; greenish cherty pebbles which are so noticeable on weathered surfaces are not plentiful.



The variation in lithology of the pebbles in the Lower Narrabeen conglomerate can be shown thus:

<i>Types of Pebbles.</i> (Percentage by Number.)						
	Quartz.	Jasper.	Chalcedony.	Sedimentary.	Acid Igneous.	
Upper .. ..	10	7 (57)	50	30	$\frac{1}{2}$	
Middle .. ..	—	13 (55)	42	30	10	
Lower .. ..	1 $\frac{1}{2}$	9 (59)	50	34	5	

These figures are the averages of only a limited number of samples, but the ratio of jasper plus chalcedony to sedimentary rocks appears to be rather constant, and can be taken as characteristic of these beds.

Table 3 gives the distribution of sizes of the pebbles for the same samples and the variation in proportion of pebbles to matrix. It is unsafe to generalise from few samples, but the basal part of these beds appears to have a larger pebble content than the upper.

The mean roundness and mean sphericity are given in Table 4. Although the first impression given by the pebbles is that of roundness, close examination of the edges indicates that the rounding is only moderate when compared with Krumbein's roundness images (1941, Pl. 1). Individual pebbles may reach a roundness of 0.8 or 0.9, but the mean is between 0.42 and 0.56, with one sample, N9, having a roundness of only 0.27, which indicates sharp broken edges (care was taken during the initial crushing not to break pebbles so that this figure is a natural one).

The shape of the pebbles, given as mean sphericity, is much more uniform than the roundness; it varies between 0.71 and 0.78, the pebbles falling into Zingg's (1935) spherical class, with the exception of N8 and N11, which are disc-like. The pebbles measured were largely chalcedony, which, being homogeneous, would tend to assume a spherical form rather than any other.

#### Permian Conglomerates.

The Permian conglomerates are represented by samples G1 and G2 from the Upper Coal Measures, G13 from the Branxton Beds, G16 from the Muree Beds, and G17 from the Greta Coal Measures (see Table 1). The distribution and lithology of these formations in the Upper Hunter River Valley has been described by Raggatt (1929; 1938). The Muree Beds have the greatest surface area.

The lithology of these samples is given in Table 5. The Upper Coal Measure beds are characterised by the absence of quartz and jasper, the limited quantity

TABLE 5.  
*Lithology of Pebbles in the  $-1+\frac{1}{2}$  in. Grade from Permian Conglomerates.*  
(Percentage by number.)

Sample No.	..	..	..	G1.	G2.	G13.	G16.	G.17
Rock types—								
Quartz .. ..	..	..	..	—	—	—	9	—
Jasper .. ..	..	..	..	—	—	21	27	—
Chalcedony and chert	..	..	..	3	7	10	5	39
Sedimentary*	..	..	..	16	3	40	59	18
Quartzite .. ..	..	..	..	—	7	—	—	2
Acid igneous†	..	..	..	81	69	28	—	24
Basalt .. ..	..	..	..	—	14	1	—	—

\* Sedimentary rocks include claystone, sandstone (fine and coarser), indurated shale,

† Acid igneous rocks include rhyolite, felsite and allied types.

of chalcedony, the rather small quantity of sedimentary rock pebbles, and the preponderance of acid igneous rock pebbles. The basalt pebbles in G2 may be due to contamination. The sample from the Branxton Bed is characterised by jasper and chalcedony, but the most prominent constituent is sedimentary

TABLE 6.  
*Size Composition of Pebbles in the Permian Conglomerates.*  
(Grade units in inches; percentage by weight.)

Grade .. ..	$-2+1.$	$-1+\frac{1}{2}.$	$-\frac{1}{2}+\frac{1}{4}.$	$-\frac{1}{4}+\frac{1}{8}.$	$-\frac{1}{8}$ (Coarse Sand and Matrix).
Sample No.—	%	%	%	%	%
G1 .. ..	20.0	13.0	41.0	18.0	8.0
G2 .. ..	66.4	25.1	4.0	1.1	3.3
G13 .. ..	52.5	35.7	11.8	—	—
G16 .. ..	9.6	19.0	47.8	4.2	19.1
G17 .. ..	24.5	28.6	37.6	7.0	2.2

TABLE 7.  
*Roundness and Sphericity of Pebbles from the Permian Conglomerate*  
( $-1+\frac{1}{2}$  inch Grade).

Sample No.—	Mean Roundness.	Mean Sphericity.	Zingg Classification.*
G1† .. ..	0.50	0.78	11
G2† .. ..	0.55	0.77	11
G13 .. ..	0.49	0.86	11
G16 .. ..	0.44	0.76	11
G17 .. ..	0.55	0.77	11

\* The shape of pebbles in Zingg's classification is : Class I, discs; Class II, spherical; Class III, blades; Class IV, rod-like.

† Acid igneous rock pebbles; the remainder are jasper and chalcedony pebbles.

TABLE 8.  
*Lithology of Pebbles in the  $-1+\frac{1}{2}$  in. Grade of River Terrace Soils.*  
(Percentage by Number.)

Sample No. .. ..	G3.	G4.	G5.	G6.	G7.	G8.	G9.	G10.	G11.	G12.	G14.	G15.	G18.
Rock types—													
Quartz .. ..	3	5	3	—	4	4	5	2	16	6	—	2	6
Jasper .. ..	4	10	15	—	8	14	15	—	26	4	2	31	29
Chalcedony and chert	37	75	64	69	40	79	54	6	35	67	42	31	9
Sedimentary* .. ..	13	3	3	15	9	2	12	13	11	14	22	21	1
Quartzite .. ..	—	—	—	—	—	—	—	—	—	—	—	—	1
Acid igneous† .. ..	29	6	10	16	33	—	12	34	12	8	29	14	27
Basalt .. ..	12	1	3	—	5	1	3	37	2	—	4	—	26

\* Sedimentary rocks include claystone, sandstone (fine and coarser), indurated shale.

† Acid igneous rocks include rhyolite, felsite and allied types.

rock; acid igneous rock pebbles are also prominent. The Muree Bed contains quartz, jasper, chalcedony and sedimentary pebbles but no acid igneous rocks, whereas the Greta Coal Measure conglomerate has conspicuous igneous rock pebbles with no quartz and jasper, although chert and chalcedony pebbles are plentiful.

The variation in size of the pebbles is given in Table 6. G2 (Upper Coal Measures) and G13 (Branxton Beds) are fairly well graded, but the pebbles of other samples are not. In G2 and G13 the maximum grade is in the  $-2+1$  inch grade. A slight maximum occurs in the other samples in the  $-\frac{1}{2}+\frac{1}{4}$  inch grade. The percentage of coarse sand and matrix is conspicuous only in G16 (Muree).

The mean roundness and sphericity are given in Table 7. The mean roundness varies from 0.44 (Muree) to 0.55 (Upper Coal Measures and Greta). The sphericity varies from 0.77 (Upper Coal Measures and Greta) to 0.86 (Branxton). The pebbles from all these samples fall into Zingg's (1935) spherical class.

#### River Terrace Soils.

The soils from which pebbles were obtained are described in the Introduction. All the samples with the exception of G10 were from Red-brown Earth on the river terraces.

The lithology is given in Table 8, which is a simplification of the rock types actually recorded, which are: quartz (milky), chalcedony and chert (red, white, grey, banded), jasper, quartzite, shale (white, grey, indurated), sandstone (coarse, fine, brown, yellow, ferruginous, clayey, chalky), claystone, ferruginous mudstone, tuff, acid igneous (mainly lavas; coarse, fine, altered, white, pale green, banded), rhyolite, porphyry, basalt, weathered basalt. There is thus a much greater variety in the gravels than in the Lower Narrabeen conglomerate.

Quartz is present in all but two of the samples in small amounts only, and is conspicuous (16%) in G11 collected from above the Upper Coal Measures.

Jasper and chalcedony are prominent constituents in all the samples except G10. The range is from 38% to 93% (G8 from near Scone). G3, G7, G14, G18 are low in jasper and chalcedony and high in acid igneous rocks (when compared with other samples from the area):

	G3.	G7.	G14.	G18.
	%	%	%	%
Jasper and chalcedony	41	48	44	38
Acid igneous ..	29	33	29	27

These samples were all collected from above the Upper Coal Measures and Branxton Beds whose jasper and chalcedony contents are rather low and acid igneous rock contents rather high. It may be presumed therefore that the parent material of the soil is in part at least the underlying rock.

Of those samples with a high percentage of jasper and chalcedony a number contain varying percentages of acid igneous rock pebbles up to 12% in G9 and G11. The large amount of jasper and chalcedony appears to have been added to the original weathering product of the Upper Coal Measures and other beds, although contamination with material from the Muree Beds might have the same effect.

Sedimentary rock pebbles occur in practically all of these samples and their source could be any of the Permian beds in the valley. Table 5 shows that the Muree beds contained nearly 60% of this type of pebble. The largest percentages of sedimentary rock pebbles occur in those samples rather low in jasper and chalcedony and therefore strengthens the case for rather less contamination of these samples.

Basalt pebbles occur in small amounts in a number of these samples, G18 containing 26% and G3, 12%. G6, G12 and G15 contain no basalt, and the remaining samples only small amounts. In view of the fact that one of the

TABLE 9.  
*Size Composition of Pebbles in the River Terrace Soils.*  
(Grade units in inches; percentage by weight.)

Grade .. .. .	$-2+1.$	$-1+\frac{1}{2}.$	$-\frac{1}{2}+\frac{1}{4}.$	$-\frac{1}{4}+\frac{1}{8}.$	$-\frac{1}{8}$ (Coarse Sand and Fine Sand).
Sample No.—	%	%	%	%	%
G3 .. .. .	42.2	21.0	25.0	6.4	5.4
G4 .. .. .	44.8	25.0	21.7	4.0	4.3
G5 .. .. .	4.1	16.8	26.0	15.9	35.2
G6 .. .. .	33.0	37.4	18.5	4.8	6.3
G7 .. .. .	57.8	21.5	11.6	2.7	4.7
G8 .. .. .	26.5	23.4	44.8	7.0	7.6
G9 .. .. .	55.5	30.3	11.1	1.0	1.9
G10 .. .. .	62.5	26.1	6.2	1.4	4.0
G11 .. .. .	27.5	32.0	32.1	7.7	—
G12 .. .. .	57.5	23.1	14.3	2.5	2.4
G14 .. .. .	91.3	8.7	—	—	—
G15 .. .. .	47.7	19.1	17.6	5.6	10.9
G18 .. .. .	76.0	24.0	—	—	—

Upper Coal Measure conglomerates contained basalt pebbles it seems probable that little significance can be attached to small quantities of basalt in these samples, whereas large quantities indicate either proximity to basaltic flow remnants, plugs or sills, or to addition by stream transport of pebbles from an

TABLE 10.  
*Roundness and Sphericity of Pebbles from the River Terrace Soils ( $-1+\frac{1}{2}$  in.  
Grade; Jasper and Chalcedony).*

	Mean Roundness.	Mean Sphericity.	Zingg Classification.*
Sample No.—			
G3 .. .. .	0.48	0.72	11
G4 .. .. .	0.48	0.73	11
G5 .. .. .	0.46	0.76	11
G6 .. .. .	0.47	0.73	11
G7 .. .. .	0.51	0.76	11
G8 .. .. .	0.53	0.77	11
G9 .. .. .	0.52	0.76	11
G10† .. .. .	0.33	0.73	11
G11 .. .. .	0.50	0.78	11
G12 .. .. .	0.51	0.73	11
G14 .. .. .	0.49	0.77	11
G15 .. .. .	0.52	0.78	11
G18 .. .. .	0.55	0.75	11

\* The shape of pebbles in Zingg's classification is: Class I, discs; Class II, spherical; Class III, blades; Class IV, rod-like.

† Acid igneous rock pebbles.

outcrop of basalt. Many of the basalt pebbles in these soils are weathered, and it is possible that many originally present may have disappeared during soil formation.

The only soil belonging to the Black Earth group (G10) contains very little quartz and chalcedony, but 37% of basaltic pebbles and 34% of acid igneous rock pebbles. As this sample was collected from near the junction of the Pages and Upper Hunter Rivers, it is possible that the basaltic pebbles have been transported there. The influence of the basalt is clearly to be traced in the formation of a Black Earth. If the basalt were *in situ*, it is probable that acid igneous rock pebbles would not be present.

The variation of sizes of the pebbles is given in Table 9. In general the pebbles are not well sorted except in G14 and G18, with a maximum of 91% and 76% in the  $-2+1$  inch grade. These are most probably river gravels, as the grading of the Permian sediments is not particularly good. G7, G9, G10, G12 also show a fairly strong maximum in the same grade. The Permian conglomerates also show a maximum in this grade, where sorting is at all good, but the Lower Narrabeen conglomerates examined here are much finer grained with a maximum in the  $-1+\frac{1}{2}$  or  $-\frac{1}{2}+\frac{1}{4}$  inch grade. Without additional samples it would be unwise to generalise further from these figures.

Figures for the roundness and sphericity are given in Table 10. The roundness for pebbles from the Red-brown earth soils varies from 0.46 to 0.55, which indicates that the edges are not at all well-rounded and that many broken pebbles are present. The mean roundness for sample G10 is only 0.33. The mean sphericity is fairly constantly high, ranging from 0.72 to 0.78. It appears to have little diagnostic value, except to indicate similarity, in this series of samples. All the pebbles fall into Zingg's spherical class. It would appear that the same kind of environment existed for all these pebbles, though the homogenous material (jasper and chalcedony) would tend to assume this shape on abrasion irrespective of environment.

#### CONCLUSIONS.

The number of samples examined was insufficient to treat the results statistically, but the following conclusions appear to be justified.

Detailed lithological examination of the various conglomerates has given precision to the description of these beds, and this information can be used to suggest the origin of the various gravelly soils which have developed on the river terraces in the area examined. Further evidence is expected from an examination of the heavy mineral residues of these soils. Contamination with material either from the Lower Narrabeen conglomerate or the resorting and redistribution of the materials of the Permian beds is indicated. Acid igneous rock pebbles appear to be derived from various members of the Permian in a number of instances. The presence of basalt pebbles indicates either nearness to source or transport from a source at no great distance. The degree of sorting of several of the terrace gravels indicates the action of rivers, but it seems that transport was not for long distances, as no pebbles from the Kuttung glacial beds were found. Little can be inferred from the figures for roundness and sphericity; the pebbles are not as well water-worn as previous descriptions indicate, which shows that transport has not been from long distances or continuous. It is probable that no further alteration of shape or roundness has been made by the action of the Upper Hunter and its tributaries. All the pebbles are of the same type except some of those in the Lower Narrabeen conglomerates which are, in addition, simpler lithologically. It is suggested that the weathering *in situ* of the Permian beds is an important factor in the soils developed on the terraces in some localities.

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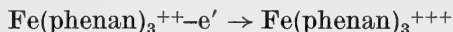
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# THE RESOLUTION OF THE TRIS o,PHENANTHROLINE FERROUS ION AND THE OXIDATION OF THE ENANTIOMORPHOUS FORMS.

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When o,phenanthroline is added to ferrous salt solutions, red compounds result which have been shown to have the constitution  $\text{Fe}(\text{phenan})_3\text{X}_2\cdot n\text{H}_2\text{O}$  (Blau, 1898). The tris o,phenanthroline ferrous ion is reversibly oxidisable to the blue tris o,phenanthroline ferric ion the redox potential for the reaction



being 1.12 volts (Smith and Richter, 1944; Dwyer and McKenzie, 1947). In this paper the resolution of the ferrous complex and the oxidation of the enantiomorphous forms is described.

The resolution was carried out through the antimonyl tartrates, and it was found that on adding potassium antimonyl tartrate to a racemic solution of  $\text{Fe}(\text{phenan})_3^{++}$  in water the l-complex d-antimonyl tartrate separated as a highly insoluble precipitate, whilst the d-complex remained in solution and could be precipitated from the mother liquid as the sparingly soluble perchlorate. The perchlorate of the laevo form was obtained by dissolving the antimonyl tartrate precipitate in caustic soda solution (thus destroying the antimonyl tartrate radicle) and adding sodium perchlorate. The active perchlorates were more soluble in water than the racemate.

The resolution of the analogous tris o,phenanthroline ruthenium II and nickel II complexes and recently that of the osmium II complex has been carried out in a similar way (Dwyer and Gyarfás, 1949*a, b, c*). In all of these complexes the d-Me(phenan)<sub>3</sub> d-antimonyl tartrate (Me=Ru II, Ni II, Os II), formed the highly insoluble compound. It is reasonable to suppose, therefore, that the form of the ferrous complex precipitated as the d-antimonyl tartrate has the same configuration as the dextrorotatory Ru II, Ni II and Os II complexes. The sign of the rotation is of no significance since all these ions possess a strongly abnormal rotatory dispersion, the investigation of which is now being carried out, and will be published in a subsequent communication.

The optical forms were more stable than the active forms of the tris 2:2' dipyridyl ferrous ion resolved by Werner (1912*a*). Thus whilst the rotations of solutions of this substance dropped to half of its original value in half an hour the phenanthroline complexes in solution have a half life of approximately one hour, and the solids possess some rotation even after a period of six months. The same relation was found between the stabilities of the corresponding  $\text{Ni}(\text{dipy})_3^{++}$  and  $\text{Ni}(\text{phenan})_3^{++}$  complexes (Morgan and Burstall, 1931; Dwyer and Gyarfás, 1949*b*). On standing from a racemic solution of the ferrous complex containing excess antimonyl tartrate, the whole of the complex precipitated slowly as the l-complex d-antimonyl tartrate, leaving a colourless solution behind. This is due to the racemisation of the solution. The equilibrium between the d and l complex ions is being shifted towards the latter, which is continuously eliminated from the solution as the insoluble antimonyl

tartrate, and finally none of the d-complex remains. A similar reaction was, observed on the resolution of the trioxalato chromiates with strychnine (Werner 1912b).

In a previous paper (Dwyer and Gyarfás, 1949a), the oxidation of the enantiomorphous forms of the tris o,phenanthroline ruthenium II complex was described. It was found that on oxidation of the active solutions of this complex the solutions of the blue ruthenium III complex were still optically active, although the magnitude of rotation was different, and that on reduction the ruthenium II complex was obtained with its rotation unchanged. If the same experiment is carried out on the active tris o,phenanthroline ferrous ion at room temperature, as stated by the authors in a note in *Nature* (Dwyer and Gyarfás, 1949), the rotation is lost on oxidation due to the rapid racemisation of the ferric complex. However, at 6° C. the rate of racemisation being reduced, active solutions of the ferric complex could be obtained. The rate of racemisation even at 6° C. was too rapid to permit measurement of the specific rotation with any degree of accuracy, but it is approximately 60% of that of the ferrous complex in the NaD line.

### EXPERIMENTAL.

Owing to the racemisation of the active substances standard solutions could not be made up for measurements of rotations. The determinations of specific rotations was done by shaking the active substance in ice-cold water for a few seconds, filtering off the undissolved material on the filter pump, and measuring the angle of rotation immediately. The concentration of the solution was determined subsequently by comparing it with a standard solution in a photo-electric colorimeter.

A 2 dm. tube was used in all experiments.

#### *l-Tris o,Phenanthroline Iron II d-Antimonyl Tartrate Tetrahydrate.*

d,l Tris o,phenanthroline ferrous sulphate was prepared by the addition of finely divided o,phenanthroline monohydrate (2.2 g.) to a solution of ferrous sulphate heptahydrate (1.2 g.) in water (100 ml.). The mixture was stirred until the phenanthroline had dissolved completely. To the deep red solution of tris o,phenanthroline ferrous sulphate a solution of potassium d-antimonyl tartrate (2.5 g.) in water (20 ml.) was added slowly. On scratching the sides of the vessel a dark red crystalline substance was obtained. The reaction mixture was cooled rapidly in ice and the precipitate filtered off immediately. The crystalline substance was found to be pure l-tris o,phenanthroline ferrous d-antimonyl tartrate. It was practically insoluble in water but could be recrystallised by solution in 0.1 N caustic soda (50 ml.) and reprecipitation with the addition of acetic acid and a little potassium antimonyl tartrate. The substance crystallised in dark red needles.

A 0.0100% solution in water gave  $\alpha_D = -0.19^\circ$ , whence  $[\alpha]_D^{25} = -950^\circ$ .

Found: Fe = 4.37%; Sb = 19.54%.

Calculated for  $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{SbO}_2\text{C}_4\text{H}_4\text{O}_6)_2 \cdot 4\text{H}_2\text{O}$ : Fe = 4.50%; Sb = 19.63%.

#### *l-Tris o,Phenanthroline Iron II Perchlorate Trihydrate.*

The l-tris o,phenanthroline ferrous d-antimonyl tartrate was dissolved in approximately N/20 caustic soda (50 ml.) by shaking at about 5° C., and the solution filtered. Sodium perchlorate solution was then added slowly and on scratching the sides of the vessel a red crystalline precipitate was obtained. This, after immediate filtration, washing with ice water and drying, gave the pure l-perchlorate in microprismatic needles. The substance was appreciably soluble in water, very soluble in acetone and sparingly soluble in alcohol.

A 0.0144% solution in water gave  $\alpha_D = -0.41^\circ$ , and a 0.0126% solution in water gave  $\alpha_D = -0.355^\circ$ , whence  $[\alpha]_D^{25} = -1416^\circ$ .

Found: Fe = 6.53%; N = 10.04%.

Calculated for  $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ : Fe = 6.58%; N = 9.90%.



*d-Tris o,Phenanthroline Iron II Perchlorate Trihydrate.*

The mother liquid of the original precipitate with potassium antimonyl tartrate was strongly dextrorotatory. The cold solution (5° C.) was treated immediately with sodium perchlorate solution. (Avoiding an excess to prevent the precipitation of potassium perchlorate.) The resulting red crystalline precipitate was the pure perchlorate of the dextro complex forming microprisms and needles.

A 0.0111% solution in water gave  $\alpha_D = +0.32^\circ$  and a 0.0123% solution in water gave  $\alpha_D = +0.35^\circ$ , whence  $[\alpha]_D^{25} = +1432^\circ$ .

Found: Fe = 6.53%.

Calculated for  $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ : Fe = 6.58%.

## SUMMARY.

Tris o,phenanthroline iron II perchlorate has been resolved through the d-antimonyl tartrate. The optical forms were stable in the solid state for some months, but racemised rapidly in solution. After oxidation of the enantio-morphous forms with ceric sulphate at 6° C., the resulting blue iron III complex was found to possess a fleeting activity.

## ACKNOWLEDGEMENTS.

The authors are indebted to Miss J. Fildes for microanalyses (N), and one of us (E.C.G.) is indebted to the Research Committee for an Assistantship.

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## A NOTE ON SOME 4-METHOXYBENZENE-AZO DERIVATIVES OF RESORCINOL

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and G. K. HUGHES, B.Sc.

*Manuscript received, October 27, 1949. Read, December 2, 1949.*

On coupling molar equivalents of diazotised p-anisidine with resorcinol monacetate in alkaline solution, both a mono- (I, 33%) and a bis-azo compound (II, 29%) were obtained, but no appreciable amounts of acetyl derivatives could be isolated. The same two products were also isolated (I, 47%; II, 17%) by coupling molar proportions of diazotised p-anisidine with resorcinol in the presence of alkali. (I) must be 2:4-dihydroxy-4'-methoxyazobenzene.

The formation of bis-azo compounds by coupling diazotised aniline with resorcinol was first reported by Wallach and Fischer (1882) (cf. Typke, 1877; Will and Pukall, 1887). It was later found that the pH of the solution determines which of two bis-azo isomers is formed. In the presence of sodium carbonate or acetate, 2 moles of diazotised aniline couple with one of resorcinol to give 2:4-bis(benzeneazo)-1:3-dihydroxybenzene (Kostanecki, 1888; cf. Liebermann and Kostanecki, 1884; Kostanecki, 1887; Orndorff and Ray, 1907), whilst in dilute excess sodium hydroxide 4:6-bis(benzeneazo)-1:3-dihydroxybenzene is formed (Kostanecki, 1888).

It is thus reasonable to assume that the structure of the bis-azo compound (II) formed above is 4:6-bis(4'-methoxybenzeneazo)-1:3-dihydroxybenzene.

On coupling molar proportions of diazotised p-anisidine with resorcinol monomethyl ether, two compounds  $C_{14}H_{14}O_3N_2$  are formed (cf. Hodgson *et al.*, 1934). One isomer, m.p. 116°, occurs to about 90%, the other, m.p. 134°, to about 10% in the mixture. Separation was achieved by exhaustive steam distillation, the higher melting isomer being slightly volatile. This isomer probably identical with the hydroxyazo compound, m.p. 121° (crude), isolated by Cumming and Ferrier (1925) from 4:4'-dimethoxyazoxybenzene by the action of light, is therefore 2-hydroxy-4:4'-dimethoxyazobenzene (III). The other isomer, m.p. 116°, would then be 4-hydroxy-2:4'-dimethoxyazobenzene (IV).

On methylation with diazomethane of (I) yields of (III) (68%) and (IV) (26%) were obtained. This result is to be expected from a hydrogen bonded o-hydroxyazo compound.

### EXPERIMENTAL.

*4'-methoxy-2:4-dihydroxyazobenzene* (I), and *4:6-bis(4'-methoxybenzeneazo)-1:3-dihydroxybenzene* (II)

(A) p-Anisidine (1 mol.) was diazotised in hydrochloric acid (3 mol.) in the usual way, and added to a freshly prepared dilute solution of resorcinol monacetate (1 mol.) in sodium hydroxide (5 mol.) at 0° C. After stirring for 30 min., the solution was made faintly acid, and the red-brown precipitate filtered off. Extraction with hot 20% acetic acid removed (I), which crystallised out on cooling, and after recrystallisation from dilute acetic acid, formed glistening carmine needles (33%), m.p. 150°, which became dull orange needles, m.p. 150–151°, on drying in the desiccator, or at 110°.

Found: N, 11.8; -OMe, 12.9%.

Calculated for  $C_{13}H_{12}O_3N_2$ : N, 11.5; -OMe, 12.7%.

The residue (II) crystallised from glacial acetic acid in minute brown-violet flakes, m.p. 225°, yield 29%.

Found: N, 14.8; -OMe, 16.1%.

Calculated for  $C_{20}H_{18}O_4N_4$ : N, 14.8; -OMe, 16.4%.

(B) Preparation as above, using resorcinol instead of its monacetate. Yields: (I), 47%; (II), 17%.

#### 4 : 6-Bis(4'-methoxybenzeneazo)-1 : 3-dimethoxybenzene (V).

(V) was formed by methylation of (II) in boiling acetone solution with excess methyl iodide in the presence of potassium carbonate. It formed red needles from dilute acetic acid.

Found: N, 13.8%.

Calculated for  $C_{22}H_{22}O_4N_4$ : N, 13.8%.

#### 2-Hydroxy-4 : 4'-dimethoxyazobenzene (III) and 4-hydroxy-2 : 4'-dimethoxyazobenzene (IV).

Preparation as for (I) and (II), using resorcinol monomethyl ether instead of resorcinol monacetate. Before acidification, the solution was extracted with ether, which removed a small quantity of red crystals of (III) (m.p., after one crystallisation from aqueous acetic acid, 127–128°). Another crop of (III) (total 5%) was obtained by acidification of the liquor, followed by exhaustive steam distillation. (III) forms glistening red monoclinic crystals from aqueous alcohol or dilute acetic acid, m.p. 134°.

Found: N, 10.8%.

Calculated for  $C_{14}H_{14}O_3N_2$ : N, 10.9%.

It is only slightly soluble in cold 0.5% to 10% sodium hydroxide solution.

The steam distillation residue affords (IV) (60%) after three crystallisations from aqueous acetic acid, aqueous alcohol or aqueous pyridine. From the former it crystallises in red needles, m.p. 85°, which after drying lose their solvent of crystallisation and become dull salmon coloured, m.p. 116°.

Found: N, 11.0%; -OMe, 23.9%.

Calculated for  $C_{14}H_{14}O_3N_2$ : N, 10.9%; -OMe, 24.3%.

The benzoyl derivative crystallises from dilute acetic acid in shimmering orange-brown flakes, m.p. 144.5°.

Found: N, 7.8%; -OMe, 16.7%.

Calculated for  $C_{21}H_{18}O_4N_2$ : N, 7.7%; -OMe, 17.1%.

#### Methylation of (I).

(I) (0.25 g.) in dry ether (50 ml.) was treated with a solution of a large excess of diazomethane (from nitrosomethylurea, 2 g.) in ether (50 ml.), and allowed to stand overnight. The filtered solution was extracted three times with 10% sodium hydroxide solution (20 ml.). The alkali extract afforded (IV) (impure, 0.07 g., 26%), the ether extract (III) (pure, 0.18 g., 68%).

#### ACKNOWLEDGEMENTS.

The authors' thanks are due to Miss J. Fildes and Mrs. E. Smith for the analyses (semi-micro) recorded in this paper, and to the Commonwealth Research Grant Committee of this University for a scholarship awarded to one of them (P.H.G.).

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# STUDIES IN THE DEMETHYLATION OF THIOANISOLE.

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*Manuscript received, November 15, 1949. Read, December 7, 1949.*

During attempts to prepare the sulphur analogues of the synthetic sex hormones stilbestrol, hexestrol and dienestrol it was not found possible to demethylate the intermediate methyl ethers and experiments were begun on the dealkylation of thioanisole (Hughes and Thompson, 1948). This paper reports further attempts using the methods successfully used with oxygen alkyl ethers.

Sodium in boiling pyridine, as used by Prey (1943) for the cleavage of phenol ethers, gave 60% thiophenol and no thioanisole was recovered.

Heating with aluminium chloride caused some demethylation, but the yields of thiophenol were low and were difficult to reproduce. With equimolecular amounts of thioanisole and aluminium chloride at 100° C. the yield of thiophenol averaged 20%, in one experiment 35% was obtained. Thioanisole was always recovered mixed with higher boiling fractions, which may contain alkylated thioanisoles (*cf.* Baddeley, 1944).

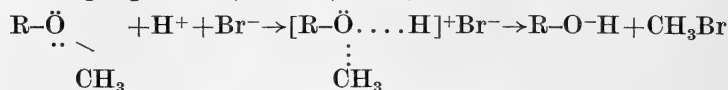
The stability of aliphatic sulphides to aluminium chloride has previously been noted by Lee and Dougherty (1939), who found that *n*-amyl sulphide was unaffected by two hours' refluxing with aluminium chloride in benzene solution. Auwers and Arndt (1909) were unable to demethylate 2-aceto-4-methyl thioanisole with aluminium chloride, but Harnish and Tarbell (1948) showed that the more labile phenyl benzyl sulphide gave 21% debenzylation when treated at 50° C. for twenty-four hours with the same reagent.

Alcoholic potash which demethylates anisole slowly at 200° C. had no appreciable effect on thioanisole after seven hours at 230° C.

Thus from the above and previous results (Hughes and Thompson, *loc. cit.*) it is obvious that thioanisole is much more resistant to both acidic and basic reagents than is anisole. The effects of the reagents used are shown in the following table.

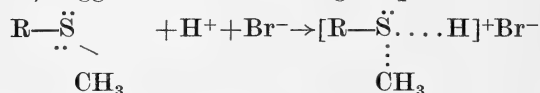
Reagent.	Reaction Conditions.	Percentage Yield of Demethylated Product.	
		Anisole.	Thioanisole.
Hydriodic acid, hydrobromic acid ..	2 hr. 130° C.	100	0
Pyridine hydrochloride .. ..	6 hr. 200° C.	100	0
Magnesium iodide .. .. .	1 hr. 200° C.	58	0
Aluminium chloride .. .. .	2 hr. 100° C.	100	20
Caustic potash in ethanol .. ..	7 hr. 200° C.	7	0
Sodium in pyridine .. .. .	5 hr. 120° C.	94	62
Sodium in ammonia .. .. .	7 hr.	27	100
	15 hr.	(Birch, 1947) 100	100

The generally accepted mechanism for acid demethylation of ethers is shown in the following equation (Remick, 1942).

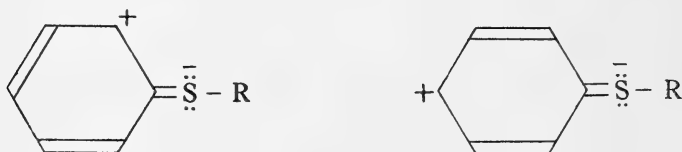


The proton addition is based on the well-known existence of  $\text{H}_3\text{O}^+$  and  $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{HCl}$ .

However, the properties of divalent sulphur reveal that proton addition is extremely weak and the slight evidence for the existence of compounds such as  $(\text{C}_2\text{H}_5)_2\text{S} \cdot \text{HCl}$  and  $\text{H}_3\text{S}^+$  (Bagster, 1911; Jableczynska-Jedrzejska and Groyecka, 1937) suggests that the analogous process

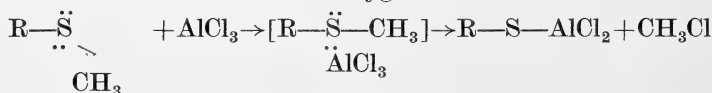


would be much less likely, and if this is the rate controlling step, then the reaction would be very slow. Furthermore, Fehnel and Carmack (1949) have presented evidence for the polarisation of the phenylmercapto group in which the benzene ring acts as an electron donor to the sulphur atom as shown in the following structures.

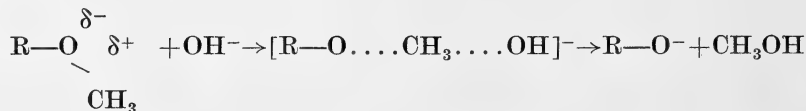


This would compensate for any loss of electron density on the sulphur atom (after the addition of the proton) and thus prevent the weakening of the sulphur carbon bond. Resonance involving these structures cannot occur with ethers as oxygen cannot expand its valency shell.

However, it is well known that sulphides co-ordinate readily with alkyl halides to form sulphonium salts while there is apparently no evidence for a similar reaction with ethers; sulphides also co-ordinate readily with oxygen to form sulphoxides and sulphones, and with halides of mercury and platinum metals, and it is reasonable to assume that this is why aluminium chloride will split thioethers, although here too the weakening of the sulphur-carbon bond is much less than is the case with the oxygen-carbon bond.



With alcoholic alkali the effective reagents must be the hydroxyl or ethoxyl ions which exert a nucleophilic attack on the carbon atom. The greater polarity of the carbon atom in anisole, due to the greater electron attracting power of oxygen, should make it more easily attacked, which is in accord with the experimental results.



(If this is the mechanism for the alkaline hydrolysis it is difficult to understand why anisole metalates in the *ortho* position with butyl lithium, whereas thioanisole undergoes lateral metalation (Gilman and Webb, 1940)).

The difference in the stability of the sulphur and oxygen alkyl linkages suggested the possibility of the transfer of the methyl group from anisole to thiophenol. As expected, when anisole and thiophenol were heated in the presence of hydriodic acid no transfer occurred, the anisole being demethylated in the normal way.

However, in the presence of alcoholic potash the thiophenoxide ion caused complete demethylation of anisole after six hours' heating at 200° C. In the absence of thiophenol the yield of phenol under the same conditions was only 7%. Stoemer and Kahlert (1901) obtained 12% phenol after fifteen hours.

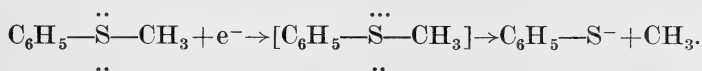
The reaction apparently involves a nucleophilic attack on the carbon atom and proceeds as follows because none of the otherwise expected intermediate products will methylate thiophenol under these conditions, and although the reaction was carried out in ethanol only thioanisole was obtained.



The reaction is applicable to methyl ethers other than anisole. Hexestrol and stilbestrol dimethyl ethers were both quantitatively demethylated in the presence of thiophenol and alcoholic potash after four hours heating at 200° C. Thioanisole was obtained as before and in the absence of thiophenol the yield of the phenols was very low. With stilbestrol dimethyl ether no addition of thiophenol across the double bond occurred. This is in agreement with the findings of Posner (1905), who under a variety of conditions could not obtain an addition product from thiophenol and stilbene.

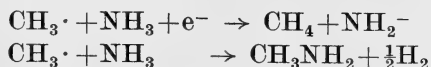
Although thioanisole is much more resistant to acidic and basic reagents than anisole, sodium in liquid ammonia, which rapidly and quantitatively splits thioanisole (Hughes and Thompson, 1948) has but a slow action on anisole (Birch, 1947; Hughes and Thompson, *loc. cit.*).

The mechanism for this reaction must therefore differ from those of the acid and basic reagents. Sodium in liquid ammonia behaves as a solution of metal cations and solvated electrons in equilibrium with metal atoms (Kraus, 1921) and consequently could be expected to react by electron addition. The ability of the sulphur atom to expand the number of electrons in its valency shell (oxygen cannot) would facilitate the formation of a transition state in the case of thioanisole.



With anisole the reaction is much slower, but quantitative. Thus we have found that increasing the reaction time from seven hours to fifteen hours increases the yield of phenol from 27% (Birch, *loc. cit.*) to 100%.

The formulation of the transition state by the addition of two electrons with the separation of two anions (Birch, *loc. cit.*) appears less likely than the addition of one electron followed by formation of the thiophenoxide ion and the free methyl radical. The latter would rapidly react with an ammoniated electron or an ammonia molecule to form methane and an amide ion, or methylamine and hydrogen respectively.



In a quantitative experiment Williams and Gebauer-Fuelnegg (1931) isolated ethane from the reaction between diethyl sulphide and sodium in liquid

ammonia and the yield of sodamide and ethane (approx. 75%) compared with the yield of sodium ethyl sulphide (95%) suggests that both these reactions may occur.

Kraus (1923) has noted the stability of aliphatic ethers to this reagent.

#### EXPERIMENTAL.

##### *Demethylation of Thioanisole by Sodium in Pyridine.*

To a stirred solution of thioanisole (12.4 g.) in refluxing dry pyridine (50 ml.) was added small pieces of sodium, the reaction being conducted in a stream of nitrogen. The solution rapidly turned purple and became progressively darker and more viscous.

After five hours the mixture was treated with aqueous pyridine to remove unreacted sodium, diluted with water and extracted with ether to remove any unchanged thioanisole.

The aqueous solution was acidified with hydrochloric acid and extracted with ether. The ether extracts after filtering to remove suspended matter were washed with water and dried over calcium chloride. Removal of the solvents by fractionation followed by distillation of the residue gave thiophenol (6.5 ml., 62%; b.p. 169–172° C.).

No thioanisole was recovered from the ether extract of the acid solution.

Under the same conditions Prey (*loc. cit.*) isolated 94% phenol from anisole.

##### *Demethylation of Thioanisole by Aluminium Chloride.*

Thioanisole (10 g.) and powdered anhydrous aluminium chloride (11 g.) were heated on a water bath for periods ranging from two to seven hours. During this time the mixture darkened in colour and sulphur containing vapours were evolved which turned lead acetate paper black.

The mixture was poured on to ice, treated with hydrochloric acid and extracted with ether. The ether layer was extracted several times with caustic soda solution and the alkaline extracts acidified and extracted with ether. After washing and drying over calcium chloride both ether extracts were carefully distilled using a fractionating column (both thiophenol and thioanisole are appreciably volatile in ether).

The yields of thiophenol were usually low and thioanisole was recovered together with other neutral products of high boiling point.

The yield of thiophenol varied from 7% to 35% (b.p. 169–172° C.) and no other substance was isolated from the alkali-soluble fraction.

The amount of thioanisole recovered varied from 75% to 30% (b.p. 194–196° C.)

The higher boiling fractions accounted for 10–20% of the original thioanisole, but no attempts were made to identify the substances present. Some solid substances crystallised from these fractions.

Heating the mixture at 120° C. caused considerable frothing, increased the quantity of sulphur-containing vapours evolved, and lowered the yield of thiophenol.

##### *Thioanisole and Alcoholic Potash.*

Thioanisole (12.4 g.) caustic potash (8 g.) and alcohol (40 ml.) were heated in an autoclave at 230–235° C. for seven hours. The reaction mixture was poured into water and extracted with ether. The aqueous layer was separated, acidified with hydrochloric acid and extracted with ether. After washing, drying and removal of the ether a negligible amount of oil remained.

##### *Demethylation of Anisole by Thiophenol.*

Anisole (10.8 g.), thiophenol (11 g.), caustic potash (8 g.) and alcohol (40 ml.) were heated in an autoclave at 200° C. for six hours. After cooling, water was added and the mixture extracted with ether. The ether extracts were washed with water, dried over calcium chloride and the ether fractionated off. Distillation of the residue gave only thioanisole b.p. 192–198° C. (9.6 g.). The thioanisole was further characterised by oxidation of 2 g. in acetic acid solution with a solution of potassium permanganate (4.7 g.) in water (140 ml.). The solution was decolorised with sulphur dioxide and partially neutralised with caustic soda. The white



solid (2.2 g.) which separated was filtered off and after recrystallisation from methanol melted at 87° C. and did not depress the melting point of an authentic specimen of the sulphone of thioanisole.

The alkaline solution was acidified, extracted with ether, and the ether extracts washed and dried. Removal of the ether followed by distillation gave phenol (8 g.) b.p. 182–185° C.

In a parallel experiment in which the thiophenol was omitted only 0.6 g. phenol (7%) was obtained.

Substitution of water (30 ml.) for the alcohol gave phenol (8 g.). When the reaction was carried out at 180° C. for six hours only 45% phenol was obtained, while at 150–170° C. for 24 hours 58% phenol was isolated.

Attempts were made to carry out the reaction at atmospheric pressure by refluxing with ethylene glycol or glycerol but after 18 hours no transfer of the methyl group had occurred. The reflux temperature in these experiments was only about 150° C.

Diphenyl ether was substituted for anisole in one experiment but no transfer occurred.

#### *Demethylation of Hexestrol Dimethyl Ether and Stilbestrol Dimethyl Ester by Thiophenol.*

The ether (1.5 g.), caustic potash (1.5 g.), thiophenol (2 ml.) and alcohol (20 ml.) were heated together in an autoclave at 200–210° C. for four hours. Water was added on cooling and the mixture extracted with ether.

The alkaline solution was acidified, boiled for several minutes to remove the volatile unchanged thiophenol and cooled.

The solid which separated was dried and recrystallised from benzene.

From hexestrol dimethyl ether was obtained hexestrol (1.35 g.) m.p. 184° C. It did not depress the melting point of an authentic specimen of hexestrol.

From stilbestrol methyl ether stilbestrol (1.35 g.) m.p. 169° C. was obtained, which was identified by mixed melting point.

The thioanisole isolated from the original ether extract was steam distilled and oxidised as before to the sulphone m.p. and mixed m.p. 87° C.

Parallel experiments in which the thiophenol was omitted gave only very small yields of the phenols.

#### *Demethylation of Anisole by Sodium in Liquid Ammonia.*

Anisole (9 g.) was added to ammonia (200 ml.) containing sodium (9 g.), with stirring during 15 minutes, in a flask surrounded by liquid ammonia contained in a Dewar flask. After standing 15 hours the ammonia was allowed to evaporate and crushed ice (100 g.) added as rapidly as was safe. The mixture was extracted with ether, the ammonia boiled from the aqueous solution, which was then acidified.

The phenol was extracted with ether (4×50 ml.), the solution dried, the ether removed and the phenol (7.5 g.) b.p. 181–183° C. distilled. No anisole was recovered from the ether solution.

In a similar experiment using sodium (6 g.) Birch (*loc. cit.*) obtained 27% phenol after seven hours.

#### ACKNOWLEDGEMENTS.

The authors are indebted to Andrews Laboratories for samples of hexestrol, stilbestrol and their dimethyl ethers; and to Dr. S. Angyal for helpful discussions.

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# ACTION OF PHOTOCHEMICALLY PRODUCED RADICALS ON ACETYLENE.

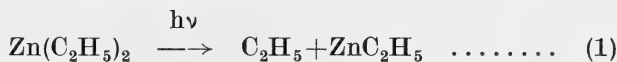
By L. E. LYONS, B.A., M.Sc.

*University of Sydney.*

*Manuscript received, November 3, 1949. Read, December 7, 1949.*

## INTRODUCTION.

The photodecomposition of zinc diethyl has been studied by Moore and Taylor (1940), who postulated the following reactions:



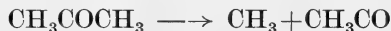
together, presumably, with



Evidence presented in this paper supports this mechanism.

It is to be noted that reaction (1) involves the liberation of free ethyl radicals from the zinc diethyl molecule, a process which must take place within one vibration period as there is a continuum in the ultra-violet absorption spectrum of zinc diethyl below 280 mμ (Thompson (1935) and Thompson and Linnett (1936)).

Now there is evidence that gaseous acetylene can be polymerised even at room temperature by the action of free radicals, e.g. by methyl radicals formed in the photolysis of acetone (Taylor and Jungers (1937)).



this phenomenon has been observed in the course of these experiments also.

Thus there was good reason to expect that the photolysis of zinc diethyl in the vapour phase would induce polymerisation of gaseous acetylene. The study of this reaction is now reported.

## EXPERIMENTAL.

*The apparatus* is illustrated in Fig. 1.

The lamp, shown at left in Fig. 1, was a high-pressure type, the discharge taking place in an inverted U-tube. The 253·7 line was reversed.

The effect of light on acetylene itself was one possible complication. The photopolymerisation of this substance has been studied by Lind and Livingstone (1930), who found a quantum yield of nine at 215 mμ. Wave-lengths much higher than this are not absorbed. Therefore, using the full light of our quartz mercury lamp, which had only a slight output in the active range, only a slight direct photopolymerisation was to be expected. Tests showed that this was negligible for our purposes.

The pressure gauge was an ordinary mercury manometer.

The presence of mercury vapour did not affect the reaction because of the absence of the 253·7 mμ line. A trap included in the line served to hold the distilled zinc diethyl before volatilisation into the reaction vessel. A Töpler

*pump* was used to collect product gases. The *zinc diethyl* was prepared and purified according to the method of "Organic Syntheses". It was stored in the dark and separated from the rest of the apparatus by two stopcocks. *Acetylene* was obtained from a cylinder and passed through sodium bisulphite and sodium hydroxide solutions and a dehydrating chain. It was also frozen and revolatilised three times, with appropriate evacuation of the last fraction each time, before being stored in a bulb. *Acetone* was purified by the method of Weissberger and Proskauer (1935), distilled into the trap, and then admitted to the reaction vessel. During a run the reaction vessel was shut off from all but the pressure gauge. Room temperature conditions were held by a stream of water over the outside of the reaction vessel. A *zinc film* appeared on the inside wall nearest

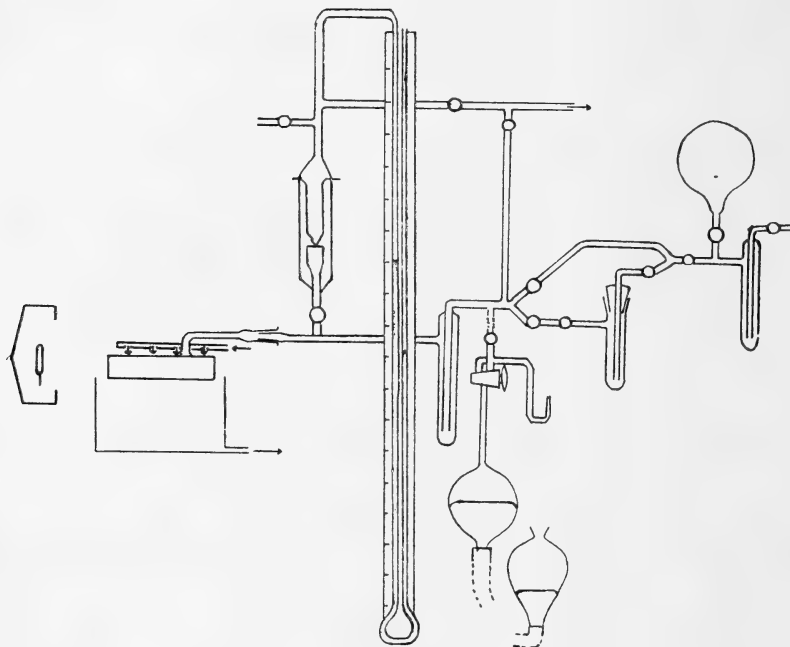


Fig. 1.

the light when zinc diethyl was used. This was estimated at the end of a run as follows: The zinc was dissolved in dilute sulphuric acid and the volume made up to 100 ml. Ten millilitres of this were made just alkaline with dilute ammonia, extracted with dithizone solution in redistilled chloroform. The chloroform extract was washed with ammonia and made up to 25 ml. This red solution was compared in a "Spekker" photoelectric colorimeter with similar preparations made from standard zinc sulphate solutions.

#### RESULTS.

(1) A film of polymer appeared on the inside of the reaction vessel whenever zinc diethyl or acetone was present with acetylene. The polymer was light-brown in colour and resembled cuprene. It was stable to heat in a vacuum. It was insoluble in ordinary organic solvents and also in concentrated nitric acid. Examination with a polarising microscope showed it to be slightly birefringent, but X-ray photographs both of a flake and of a powder made from it showed no sign of a crystal structure.

(2) Irradiation of an acetone-acetylene mixture gave results shown in Table I.

(3) Irradiation of zinc diethyl, acetylene and mixtures of the two gave results which are summarised in Table II.

In the table, results in lines 2, 3, 4, 5, 8 and 10 are all based upon independent experimental measurement. Figures in lines 6, 7 and 11 are deduced from the others. Figures in line 10 are calculated from the amount of metallic zinc deposited and found by analysis.

TABLE I.  
*Acetone-Acetylene.*  
Time of irradiation : 1130 mins. Temperature : 22° C.

	Initial Pressure. (Mm.)	Final Pressure. (Mm.)
Acetylene .. ..	137	—
Acetone .. ..	188	—
Carbon monoxide ..	—	8.3 (by analysis)
Total .. ..	325	318

TABLE II.  
*Zinc Diethyl, Acetylene.*  
Temperature : 22° C.  $\pm$  2. Pressures in mm. mercury.

1	Run .. ..	11	13	14	15	16	17
2	Time (mins.) .. ..	117	135	40	82	81	153
3	Zn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , initial .. ..	19	0	20	20	16	14.5
4	C <sub>2</sub> H <sub>2</sub> , initial .. ..	0	282	215.5	142	0	325
5	Total, final. .. ..	21.5	281	239	163	19	342
6	Zn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> + C <sub>2</sub> H <sub>2</sub> , final .. ..	—	—	206	142	—	318
7	Zn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , final .. ..	—	—	—	16.8	19	10
8	C <sub>2</sub> H <sub>2</sub> , final .. ..	—	—	—	125.5	—	308
9	Product gases .. ..	—	—	44	21	5.7	24
10	Decrease in Zn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> .. ..	—	—	—	3.2	2.7	4.5
11	Decrease in C <sub>2</sub> H <sub>2</sub> .. ..	—	—	—	16.5	—	17

*Notes.*

Run 12 discarded as analysis revealed acetylene to be impure.  
Runs 1-10 were made with an insufficiently accurate manometer  
and were discarded.

### DISCUSSION OF RESULTS.

(1) The efficiency of the free radicals from acetone in polymerising acetylene may be estimated as follows :

One molecule of carbon monoxide is formed from one molecule of acetone so that a measure of the acetone decomposed is possible. After allowing for the carbon monoxide present in the final mixture, the decrease in total pressure which was observed is a direct measure of the acetylene polymerised, since one molecule of acetone gives rise to one molecule of ethane besides the carbon monoxide. Biacetyl is not formed in the presence of a foreign gas (Iredale and Lyons (1944)).

Let  $p_{o,f}$  denote the original, final pressure, and

$p_{co}$  ,, ,, carbon monoxide pressure.

Then number of molecules of acetylene polymerised for each free radical

$$\begin{aligned} \text{produced} &= \frac{\text{Po} - \text{Pr} + \text{Pco}}{\text{Pco}} \\ &= \frac{325 - 318 + 8}{8} \\ &= 1.9 \text{ molecules/radical.} \end{aligned}$$

This agrees with the results of Taylor and Jungers (1937).

(2) The photolysis of zinc diethyl is known to give no butane at room temperatures, but only ethylene and ethane, i.e. one molecule of zinc diethyl gives two molecules of products (Moore and Taylor (1940)).

From Table II, run 16, it is seen that one molecule of zinc diethyl does give 2.1 moles of products, and so the earlier work is confirmed.

(3) In the runs where acetylene was present with the zinc diethyl, the results indicate the formation of vapour products other than from the zinc diethyl, e.g. in run 15 there were 6.7 moles of products for one mole of zinc diethyl used, and in run 17, 5.3 moles of products. The gaseous products were in every case completely condensable with liquid air, indicating that neither hydrogen nor methane was present.

As the only possible source of gaseous products apart from the zinc diethyl was the acetylene itself, it is concluded that the reaction produces from the acetylene (a) a volatile compound as well as (b) a solid polymer.

(4) The ethyl radical polymerisation efficiency may be calculated by saying that:

Number of radicals produced =  $2 \times$  number of molecules of zinc diethyl decomposed.

The results give 2.5 molecules polymerised/radical for run 15,  
and 1.9 molecules polymerised/radical for run 17.

These figures may be compared with 1.9 molecules/methyl radical (see above) for acetone-acetylene, a figure obtained by a totally different method. Thus it may be said that methyl and ethyl radicals are of about equal efficiency in polymerising acetylene.

(5) The percentage of ethyl radicals efficient in producing polymerisation may be calculated assuming a mean number of  $C_2$  units in the polymer.

For three units in the polymer, 75% of the radicals are effective polymerising agents, for four units 55% and for six, 37%. So it is seen that about one in every two radicals initiates a chain.

#### SUMMARY.

(1) Zinc diethyl photolysis involves free radicals and the previously postulated mechanism is supported.

(2) Acetylene is polymerised by methyl and ethyl radicals with about equal efficiency.

(3) The products of the polymerisation are (a) a volatile substance, and (b) a non-crystalline solid.

(4) 2.2 molecules of acetylene polymerise for each radical produced.

(5) One in every two radicals initiates a chain.

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## A FURTHER CONTRIBUTION TO THE GEOLOGY OF THE GOULBURN DISTRICT, N.S.W.

By G. F. K. NAYLOR, M.A., M.Sc., Dip. Ed.

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### PART I. EVIDENCE OF A MAJOR FOLD-STRUCTURE IN THE PALÆOZOIC ROCKS TO THE EAST OF GOULBURN.

In a paper published in this journal in 1935 (Naylor, 1935) the writer expressed the opinion that certain observed relationships between Silurian and Ordovician strata near Bungonia could best be explained by the assumption of an overfolded structure.

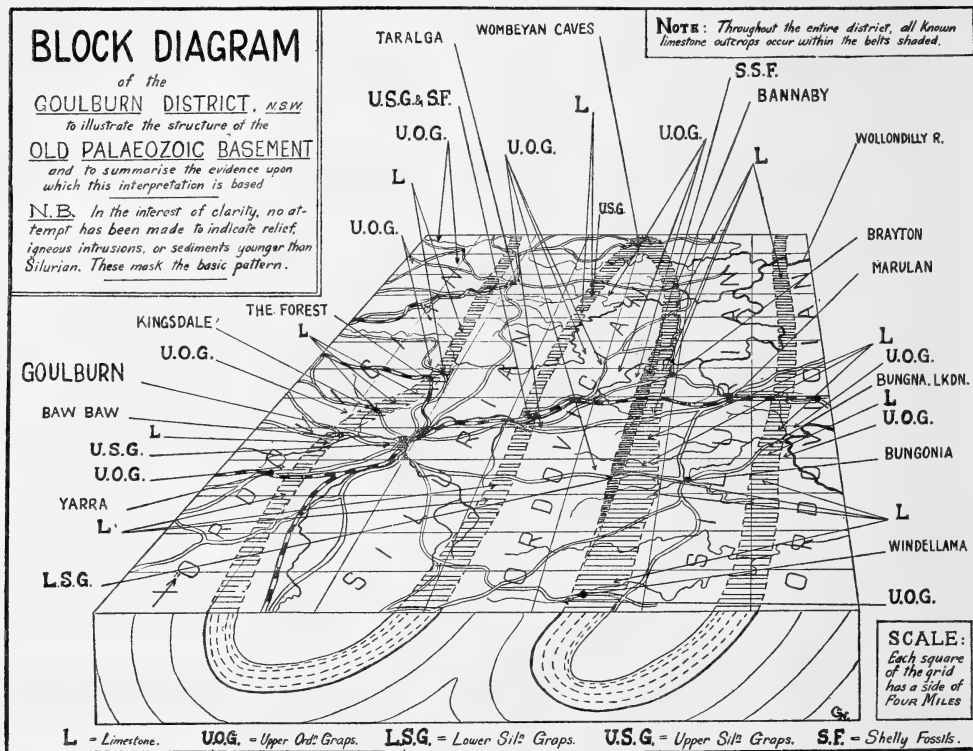
This seemed to afford the best suggestion to account for the fact that rocks with a definite Upper Ordovician graptolite fauna overlie (in the field) other strata with equally definite Lower Silurian graptolites. The evidence for the fold structure was then admittedly incomplete ; but shortly after the publication of the paper mentioned additional field work enabled many of the gaps to be filled in. The writer was preparing a further communication on this matter in 1939, but was interrupted by the war. No more field work was possible until 1945, and this tended to confirm the evidence for the fold structure, while bringing to light certain unexpected facts which render necessary a complete review of the Palæozoic sequence near Goulburn itself. It was the intention of the writer to carry out the field work necessary to attempt this review, and to publish the additional evidence for the fold structure at the same time. Since his appointment to the staff of the University of Queensland in 1946 no opportunity to renew field work at Goulburn has occurred, and may not do so for some time. Hence this opportunity is being taken to present the data at present available, for the benefit of other workers in adjoining areas. A brief mention will also be made of the evidence which appears to preclude the acceptance of the Upper Devonian age that has been traditionally assigned to the rocks in the immediate vicinity of Goulburn.

#### *Summary of Observations Previously Recorded.*

On the road section between Bungonia and Goulburn were noted rocks of Upper Ordovician age. These dipped steeply to the west and apparently overlay strata containing a Lower Silurian graptolite fauna, also dipping to the west. These in turn appeared to overlie a series of slates and quartzites including isolated patches of limestone, which were assumed, in the absence of evidence to the contrary, to be of Upper Silurian age. There was thus an apparent inversion of these three series, suggesting that they occupied the underlying limb of a great anticlinal fold, overturned towards the east. It was assumed that the Upper Silurian Series east of Bungonia represented the eastern limb of an adjacent syncline. It was further inferred from the presence of Silurian graptolites on the Marulan-Goulburn road section, that Silurian rocks were present on the western limb of the anticline, adjacent to the western boundary of the Ordovician belt. The assumed structure was indicated in a sketch section published along with the paper.

*Additional Evidence from Bungonia-Goulburn Section.*

(a) In a paper written in 1936, Garretty (1936), while agreeing generally with the structure offered above, suggested that the limestones in portions 18 and 46 ph. Jerrara, might be of Devonian rather than Silurian age, as previously assumed by the present writer. A more recent examination, however, has revealed that a bed of limestone, not outcropping at the surface, has been met in a shaft sunk a little to the north of the outcrop in portion 18. Amongst the blocks of limestone which had unquestionably been removed from the shaft and hence may be regarded as being *in situ*, were found good specimens of *Pentamerus knighti*, supporting the assumption of an Upper Silurian age for this limestone belt.



More convincing evidence of the pre-Devonian age of the limestones lies in the fact that they are metamorphosed by the Marulan batholith, while the known Devonian lies upon its eroded surface (Naylor, 1939).

(b) Thanks to information supplied by a local resident, Mr. I. Frost, limestone has been located and examined by the writer in two adjacent localities to the west of the Ordovician belt along the course of McKellar's Creek, about six miles east of Goulburn. The two outcrops of limestone occurring here do not appear to have been recorded by Carne and Jones in their survey. They are small in extent and of no economic significance. Both outcrops are marmorised by the contact effects of the adjacent porphyritic rocks, but contain numerous fossils, mainly tabulate and rugose corals, an assemblage corresponding to that of the Silurian limestones elsewhere. *Favosites* and *Heliolites* are recognisable generically but the species are indeterminate.



(c) A series of relatively soft light-bluish-grey clay-stones are met immediately to the west of the limestones on the eastern side of the Ordovician belt. From this, however, they are separated by the Lower Silurian shales of the Jerrara Beds, and hence they must be assigned to the Silurian group. Whether they should be classed as Upper or Lower Silurian is a matter of doubt, since they themselves appear to contain no fossils. However, what is presumably the same horizon has been located a little to the east of the McKellar's Creek limestone, adding to the symmetry of the distribution of the strata, and lending support to the assumption of an anticlinal fold. Additional confirmatory evidence in favour of this interpretation is offered by the distribution of the quartzitic horizon of the Silurian series.

(d) The Upper Ordovician rocks themselves show a similar tendency towards symmetrical distribution of characteristic horizons, while a zone towards the central part of the belt shows evidence of great compressive stresses such as might be expected to occur along the axis of a fold some distance below the original surface.

The corresponding rock zones on either side of this supposed axis tend to be wider to the west than to the east. However, this would appear to agree well with the conception of an over-fold in which it is reasonable to expect the upper (here western) limb to be thickened by compression, while the thickness of the lower (eastern) limb would be reduced by tension.

#### *Evidence from the Marulan-Goulburn Section.*

Proceeding west from Marulan the igneous rock is found to extend for about a mile and a half beyond the Bungonia turn-off, after which one meets relatively gently dipping quartzites and sandy shales (dip W. at 30°–40°). These may be of Upper Devonian age and consequently not immediately connected with the problem of the Ordovician and Silurian folding. However, this should not be too readily assumed. Further on, the dip of the strata is found to be steeper, reaching the 50°–80° range characteristic of the older Palæozoic rocks. Lithologically the rocks here consist of quartzites with thin interbedded bands of slate and claystone, the colour and texture of both being characteristic of those associated with the Silurian elsewhere. Just before reaching Shelley's Flat, a thick series of soft bluish-grey claystones, almost devoid of quartzites, occurs. On the eastern edge of these shales, just opposite the residence of Mr. Henderson, to whom the writer is indebted for the information, is a very small outcrop of what is probably a larger underlying mass of limestone. The small amount of limestone that is exposed is quite fossiliferous, the types including tabulate and rugose corals, not well enough preserved for specific identification.

Another small outcrop of limestone, which more closely approaches a travertine, occurs about a mile to the south, but is probably of secondary origin and hence of little immediate structural significance.

Occupying the "Flat" itself, and largely masked by alluvium, is a series of slates which seem to correspond with the Jerrara Beds, though graptolites have not been found in them in this locality. (It should be pointed out that the extent of the Jerrara series has been investigated further since the writer's earlier paper, and is now known to be at least four miles along the strike, having been traced on either side of the Bungonia-Goulburn road as far south as Bungonia Creek and as far north as Jerrara Creek. A continuation of this line would intersect the Hume Highway very close to Shelley's Flat, and pass northward a little to the west of Brayton.)

From the western edge of the Flat almost to the Carrick turn-off, a distance of about five miles, one passes over graptolite-bearing rocks of Upper Ordovician age. These are lithologically distinct from the Silurian types. Well cleaved

bluish-grey slates, quartz schists, and blue cherts predominate. The slates are much harder than those of the Silurian, especially of the Upper Silurian.

Graptolites are plentiful towards the margins, though occasionally their collection is rendered difficult by the development of cross-cleavage. A small collection taken from the Carrick Road on the western margin was submitted some years ago to Dr. D. E. Thomas, who identified the forms as belonging to an extreme Upper Ordovician horizon.

A much more extensive collection has now been made by the author from cuttings in more recently constructed deviations in the Hume Highway. Two horizons in which graptolites are particularly abundant occur on the western and eastern margins of the Ordovician belt. The graptolites in these two localities are quite well preserved, and the similarity of the assemblages shown below would appear to suggest beyond reasonable doubt that the same horizon is represented in both cases. The extreme Upper Ordovician age of this horizon is also indicated.

(a) *Forms occurring in the Western Locality.*

*Dicellograptus* sp.  
*Diplograptus truncatus*.  
*Diplograptus quadrimucronatus* var.  
*spingerus*.

*Climacograptus* cf. *rectangularis*.  
*Climacograptus* sp.  
*Leptograptus* cf. *capillaris*.  
*Diplograptus* cf. *calcaratus*.  
*Diplograptus calcaratus* var. *tenuicornis*.

(b) *Forms occurring in the Eastern Locality.*

*Climacograptus rectangularis*.  
*Climacograptus supernus*.  
*Climacograptus* sp. (other than above)  
*Diplograptus* sp.  
*Retiograptus* cf. *pulcherrimus*.  
*Dicellograptus pumilus*.  
*Dicellograptus* cf. *forchammeri*.

About 200 yards east of the Carrick Road Junction, the Ordovician strata give place to soft greyish-blue shales containing *Pentamerus knighti* and other shelly fossils, as well as recognisable *M. bohemicus*. Another hundred yards to the west are finely banded bluish-grey shales containing Upper Silurian graptolite forms (Naylor, 1935a). These shales, with interbedded quartzite, can be traced onward as far as Boxer's Creek, where they are terminated by a porphyritic intrusion about half a mile in width. Thereafter the slates continue to the foot of Governor's Hill, where there is no clear boundary between these and the arenaceous rocks that have hitherto been accepted as Upper Devonian. It can be seen from this description that the main features of the section along the Hume Highway are very similar to those of the section along the Bungonia-Goulburn road, a distance of four to six miles further south.

*Evidence from an East-West Section through Brayton.*

The sedimentary rocks to the north and west of Brayton are separated from those just described by a westward projection of the Marulan batholith, but corresponding types are found and there is no doubt of their original continuity with those of the areas just described. The relation between the Silurian and Ordovician strata near Brayton which puzzled the writer for many years becomes simplified in the light of the folding deduced from observations further south.

Adjoining the porphyritic complex near Brayton Cross-roads is an outcrop of marmorised limestone, to the west of which are hornfelses and metamorphosed tuffs, together with interbedded flows of lamprophyre. This region appears to have been a volcanic centre in Silurian times, but most of the metamorphism is

probably due to the proximity of the batholith. What may be called the "volcanic" series can be traced westward for about a mile and is succeeded first by quartzites then by a thick series of slates with very little quartzite. These extend for fully half a mile, until finally there is exposed in a creek bed a highly silicified rock containing numerous Silurian shelly fossils, in which the genus *Atrypa* predominates. (These were identified as definitely Silurian by the late Mr. Chapman.) Fifty yards beyond this point the lithology changes and the characteristic hard, cleaved, bluish-grey slates and cherts of the Ordovician series outcrop.

All the rocks here are dipping to the westward, so that the Silurian appears to underlie the Ordovician, an impression which is greatly strengthened by the fact that the fossiliferous bands on the edge of the Silurian outcrop in the creek bed, while Ordovician graptolites may be collected high above them on the hillsides.

The exact age of the Silurian rocks here is doubtful. It may be assumed with reasonable safety that the Brayton limestone is Upper Silurian, since this age has been proved for most of the limestones in this district. It is highly marmorised and fossils are very scarce. The writer is inclined to the opinion, based on lithological similarity, that the western portion of the slates corresponds to the Jerrara series and hence is of Lower Silurian age. This would imply that the fossiliferous beds adjacent to the Ordovician are also Lower Silurian—an assumption which the fossils themselves do not appear to either confirm or deny. While undoubtedly Silurian types, their exact horizon is so far indeterminate.

The Ordovician beds nearest the Silurian contain fairly well preserved graptolites, and would appear to represent the uppermost part of the Upper Ordovician system. The following forms have been collected:

*Climacograptus bicornis*.

*Diplograptus quadrimucronatus*.

*Dicellograptus complanatus*.

West of Brayton the Ordovician belt extends for about four miles to the foot of the main Cookbundoon Range, where it is unconformably overlain by the marine sediments of the Upper Devonian. Graptolites are fairly numerous throughout this region of Ordovician rocks, but there are certain marked changes in the distribution of the forms which have a distinct bearing on the present problem.

As has been pointed out, the eastern margin appears to be of very late Ordovician age. About two miles further west, however, near the Greenwich Park-Towrang Road, occur numerous graptolites of a distinctive and diminutive nature which were regarded by Dr. Thomas as being representative of the lowest part of the Upper Ordovician, and the writer's own observations seem to point to the same conclusion. The list of forms identified by Dr. Thomas are as follows:

*Dicellograptus sextans*.

*Cryptograptus tricornis*.

*Dicellograptus divaricatus* var. *angustus* (nov.).

cf. *Leptograptus*.

*Diplograptus* sp.

Further west again the fauna appear to belong to a higher zone:

*Dicellograptus elegans*.

*Climacograptus* cf. *caudatus*.

*Dicranograptus hians* var. *apertus*.

For these identifications the writer is also indebted to Dr. Thomas.

In this line of section one cannot inspect the western junction between Ordovician and Silurian series since it is overlain by the Devonian strata. However, in the same line, beyond the Cookbundoon Range, the Silurian limestones of The Forest are situated a little to the east of another graptolite-bearing Ordovician belt.

*Evidence from the Section near Kerrawary Creek and the Cookbundoon River.*

The information so far available concerning this section is not very detailed but is significant when considered in conjunction with the other sections just described.

North of Big Hill, on the southern bank of the Cookbundoon River, about two miles west of the Swallow-tail Pass, there occurs an isolated outcrop of marmorised limestone extending discontinuously for about a quarter of a mile along the western margin of the igneous intrusion that occupies so much of the country in that vicinity. No fossils other than crinoids have survived the metamorphism to which this limestone has been subjected, but its alignment corresponds to that of the Bungonia-Brayton limestone belt, and supports the assumption of its Silurian age. Further west, near the junction of the River with Kerrawary Creek, occur graptolites which are definitely Upper Ordovician types, though an exact list of forms is not available. A collection made by the writer from the western portion of this belt between Kerrawary Creek and the Bannaby-Taralga road includes the following types:

*Diplograptus calcaratus.*

*Dicellograptus* cf. *complanatus.*

*Dicellograptus complanatus* var. *ornatus.*

*Dicranograptus clingani.*

Still further westward near the junction of Kerrawary Creek and Cowhorn Gully, there is a prominent outcrop of fossiliferous Upper Silurian limestone with interbedded shales containing *Monograptus*. These have already been noted by the writer (Naylor, 1937). West of Taralga Upper Ordovician graptolites have been collected at numerous localities in the vicinity of Goldspie and Yalbraith, and at Bumaroo Ford.

*Summary of Evidence.*

It is readily admitted that the data available in any single one of these sections is, for various reasons, incomplete; but considering the evidence as a whole the conclusion that there is a major overfolded anticlinal structure in the Ordovician and Silurian rocks appears to be inescapable. What is lacking in one section is supplied from a parallel one. Thus the absence of graptolites on the western part of the Bungonia-Goulburn Section is compensated by their abundance on the corresponding part of the Marulan-Goulburn Section, where the boundary between Ordovician and Silurian strata is well defined. Similarly the absence of Upper Silurian limestone from this part of the latter section is offset by the occurrence in McKellar's Creek. The lamprophyres and breccias characteristic of the Silurian series at Brayton may or may not occur beneath the Devonian strata to the west of the Ordovician belt, but they certainly have a counterpart in the western Silurian belt between the Bungonia-Goulburn and Marulan-Goulburn roads.

*Stratigraphical Implications.*

Certain inferences concerning the sequence and relationship of the older Palaeozoic rocks may be drawn from the foregoing discussion. In the first place it would appear that the structures present are fundamentally simpler than had previously been supposed. An anticline rather than an anticlinorium

is suggested. It is true that much local folding may be observed throughout the area but this has never been traced for any appreciable distance. Moreover such folding appears to be confined to the more argillaceous sediments and may readily be attributed to "drag folding" caused by differential movement of more competent arenaceous beds on either side. These latter, as far as the writer is aware, exhibit only simple though steep dips.

If one accepts the existence of a huge and relatively simple anticline, to which the existing evidence tends to point, the folding of both Upper Ordovician and Silurian strata would appear to have resulted from the one movement. In other words the two series seem to be substantially conformable throughout. This view is supported by field evidence, since not only do both series appear to have suffered the same degree of folding, but where the junction between them can be located, no significant angular variation in the strike or dip has been observed.

Woolnough (1909), in the original paper on the Tallong-Marulan district, described an unconformity beneath the Upper Silurian limestone at Marulan, and the position of this structure has since been located exactly by Dr. G. D. Osborne. Geological opinion concerning the relations between Ordovician and Silurian in N.S.W. appears to have been considerably influenced by this occurrence, but the writer feels that it would be inadvisable to attach too much stratigraphical or structural significance to the angular nature of the exposed junction between the Marulan limestone and the underlying slates. In this locality the limestone is hundreds of feet in thickness and must have offered great resistance during the folding processes, with an almost inevitable disturbance of the original relationship between it and the adjoining less competent argillaceous beds. Moreover, the beds immediately below the limestone have never been proved to be of Ordovician age. This has merely been inferred from the assumption of unconformable relations. The writer, who has examined this locality, considers that the slates present the lithological characteristics suggestive of Silurian rather than Ordovician types, and it is significant that in no other locality have the limestones been shown to be the basal member of the Silurian series. Finally, angular discordance may be observed from Bungonia Lookdown between the base of the Upper Belt of limestone and the (presumably argillaceous) rocks which separate it from the Lower Belt.

In short, the bulk of the evidence at present available from the Bungonia-Goulburn district seems to indicate the absence of any appreciable epi-Ordovician orogeny, though the transition in many places from Upper Ordovician to Upper Silurian strata certainly implies a discontinuity of sedimentation.

Epi-Silurian folding, however, must have taken place on a grand scale, affecting both Upper Ordovician and Silurian strata, producing between Marulan and Goulburn a huge anticline which was overturned to the east. During this folding the Ordovician rocks, being more deeply buried, suffered a greater degree of dynamic metamorphism than the overlying Silurian strata. It is suggested that this accounts for the fact that the former exhibit a greater degree of recrystallisation and a more disturbed character than the latter, though the general dips of both series are equally steep.

An exception to the steep dips of the Silurian strata occurs in the immediate vicinity of Goulburn itself, where the competent nature of a large mass of quartzite appears to have exerted considerable resistance to the folding and resulted in shallower local dips (see Part II).

## PART II. EVIDENCE CONCERNING THE AGE OF THE SEDIMENTARY ROCKS AT GOULBURN.

Those responsible for compiling the State Geological Map must have had some reason for assigning a Devonian age to a large area of country surrounding

the City of Goulburn and extending eastwards towards the Shoalhaven River. In view of the fact that the great bulk of this region has now been shown conclusively to be either Ordovician or Silurian, it is difficult to be certain what the basis of the earlier classification was. As far as the writer is aware from enquiries of the personnel of the Geological Survey, the provisional assignment of a Devonian age to these rocks was largely influenced by the collection of *Lepidodendron australe* and some marine fossils with strong Lambian affinities on the summit of the Cookbundoon Range. No doubt the lithological characters of the white quartzite of the Memorial Hill and the associated conglomerates and red beds further suggested that these rocks should be regarded as Devonian.

This view was absorbed by the writer as a student and never seriously questioned by him (or as far as he is aware, by anyone else) until quite recently. However, a careful examination of the actual state of knowledge on this matter has served to convince the writer that the following are the facts of the case :

- (a) The finding of *Lepidodendron australe* and the Lambian marine assemblage on the Cookbundoon Range at several localities has been confirmed personally by the writer's own collection of these forms at points along the whole length of the Cookbundoon Range from Narrangaril Trig. Station to the vicinity of Bannaby.
- (b) Similar marine Upper Devonian fossils occur in arenaceous beds along the course of Bungonia Creek, near Bungonia. (These are the beds which have been shown by the writer (Naylor, 1939) to lie upon the eroded surface of the Marulan batholith.)
- (c) No Devonian fossils have been found closer to Goulburn than those at Narrangaril Trig.—about five or six miles N.E. of the centre of the city.
- (d) There is no record of any collection of recognisable fossils from any of the quartzites, conglomerates or shales of the Memorial Hill, Governor's Hill or the immediate surroundings. The writer has literally spent weeks in a fruitless search for fossils in these rocks.
- (e) The continuity which has always been assumed to exist between the Memorial Hill quartzites and those of the Cookbundoon Range is by no means evident when one inspects aerial photographs of this region. The strike of the undoubted Upper Devonian (fossiliferous) beds of the Narrangaril locality is seen to sweep round to the westward without crossing the Wollondilly River or the main railway line, assuming a direction almost at right angles to the trend of the great whale-back of quartzite that extends for a couple of miles N.N.E. of the big Railway Department quarry at North Goulburn. Large alluvial flats at the bend of the river obscure the actual relationships of these two rock masses at what would appear to be their point of junction.
- (f) The discontinuity suggested by the aerial photographs is supported by field inspection of the critical area on the ground. Discontinuity can hardly be proved, but seems to constitute a more reasonable assumption than continuity. Whether there is or is not continuity (i.e. with or without conformity) the field evidence leaves no doubt that the Narrangaril beds would certainly overlies the Goulburn quartzites if they did all form part of the one series.
- (g) The quartzites outcropping in the North Goulburn Railway quarry are associated with bands of something akin to a quartz schist, in which carbonaceous fragments suggestive of organic remains are here and there abundant. The late Dr. F. A. Singleton, on viewing specimens of these, unhesitatingly proclaimed them to be graptolitic. However,

the writer himself is not prepared to make this claim, as he has been unable to distinguish any signs of graptolitic structure to his own satisfaction. Nevertheless, he has collected exactly similar specimens from the point of view of lithology and carbonaceous content at points north of Murray's Flats, where the sediments underlie the Narrangaril beds, and appear to be unconformably separated from them.

- (h) A careful examination, which the writer has been enabled to carry out many times, of an east-west section from the Memorial Hill through the City of Goulburn to and beyond the water storage tanks on the top of the hill to the west of the city, leads to the conclusion that the Memorial quartzite underlies the shaly and sandy beds on which the city itself is mainly built. These are folded into a syncline whose nearly meridional axis lies slightly west of the city.
- (i) In May 1945 the writer was fortunate enough to locate a horizon within this syncline where *Monograptus bohemicus* was abundant and easily recognisable.

#### CONCLUSION.

This would appear to justify the assumption of an Upper Silurian age for the beds of the Goulburn Syncline.

While the above facts do not provide positive evidence of the exact age of the Memorial Quartzite and its associated conglomerates, it seems unlikely that they are younger than Upper Silurian. The dips of these rocks would appear to be shallow in contrast with those of the Silurian elsewhere in the Goulburn district—a fact which has no doubt contributed to the general impression of their Devonian age. However, the beds in which *Monograptus* was collected are themselves dipping gently (E. 20° S. at 30°) and in any case the Yass district provides an example of a region where the folding of the Silurian strata has been comparatively gentle over a localised area.

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# THE KUTTUNG VULCANICITY OF THE HUNTER-KARUAH DISTRICT, WITH SPECIAL REFERENCE TO THE OCCURRENCE OF IGNIMBRITES.

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## INTRODUCTION.

The Kuttung Series in N.S.W. occupies the time interval from the top of the Tournaisian (mid-Lower Carboniferous) to the base of the Permian System. Thus it is to be regarded as the upper part of the Carboniferous in this State, although the flora of the Series suggests a correlation with the Middle Carboniferous of the Northern Hemisphere rather than with the Upper Carboniferous (Walkom, 1919).

This Series was described from the Lower Hunter District and named by T. W. E. David and Sussmilch (1919), and was assumed to succeed the Lower Carboniferous Burindi Series. This region thus became known as the type-area, and later was intensively studied by Osborne (1922-1925), but subsequent researches in other districts by W. R. Browne and S. W. Carey (see 1938, p. 591) established the contemporaneity of the Lower Kuttung Series (the Basal and Volcanic Stages of Osborne) and the Upper Burindi, both of these stratigraphical units being approximately synchronous with the Viséan of Europe.

In all places in N.S.W. where the terrestrial Kuttung Series has been studied a lower dominantly volcanic section and an upper dominantly glacial section have been recognised, although evidences of vulcanism over a wide area during the Glacial Stage are forthcoming in the development of the Paterson type of toscanite-dellenite lavas, and many pyroclastic units interbedded with glacial sediments. Nevertheless, the period of the Lower Kuttung witnessed an intensive vulcanicity probably greater than that of any other Palæozoic epoch. This was succeeded, after a lapse of time and some diastrophic activity, by relatively quiet conditions with extensive clastic sedimentation in the Lower Glacial Stage of the Upper Kuttung. The Upper Glacial Stage was marked by local volcanic activity in a number of places, as at Stroud, Raymond Terrace District, Pokolbin and Stanhope, but elsewhere was characterised by accumulation of glacial sediments, with an absence of lava and true pyroclastic deposits.

In earlier papers upon the Lower Hunter and Karuah Districts, the writer dealt in detail with the stratigraphy and petrography, but refrained from



discussing critically the broader aspects and petrogenetic significance of the lava-sequences, and the mode of development and/or accumulation of the pyroclastic rocks. This policy was followed because of the imperfect state of our knowledge of the problems involved.

The present paper deals mainly with the great volcanic succession of the Lower Kuttung, although the Upper Kuttung will be considered to some extent.

The aims of the paper may be stated to be as follows :

- (a) To review the salient facts about the vulcanicity in the light of information from researches upon the *nuée ardente* type of eruption.
- (b) To describe the field occurrence and widespread distribution of the ignimbrites in the succession.
- (c) To relate the time of the ignimbrite-development to the general framework sequence of the Volcanic Stage.
- (d) To discuss the mode of origin of the deposits.

Some chemical analyses of the Kuttung lavas will be cited, and petrographic details sufficient to justify the determination of some of the rocks as *ignimbrites* will be given. However, full chemical study and critical textural and mineralogical investigations will be necessary before one can appreciate fully the remarkable vulcanicity of Carboniferous times in N.S.W.

#### FRAMEWORK SEQUENCE OF THE LOWER KUTTUNG.

##### (a) *The Lower Hunter Region.*

In 1919 (p. 288) W. R. Browne pointed out the general character of the Kuttung lava sequence, drawing attention to the main feature of a general decreasing basicity, with concentration of andesites at the base of the Volcanic Stage, of dacitic and toscanitic rocks in the central portion, and of rhyolitic types in the upper part. He gave a succinct account of the mineralogical and textural relationships of the lavas, as then known.

In 1925 the writer stated the following as the framework sequence for the Clarencetown-Paterson District (No. 1 being the oldest unit) :

7. Dacites.
6. Potash Rhyolites.
5. Toscanite-Dellenite Group (Mt. Gilmore Type).
4. Dacites.
3. Quartz Keratophyres (Williams River Type).
2. Pyroxene Andesites (Hudson's Peak Type).
1. Hornblende Andesites (Martin's Creek Type).

As pointed out by various workers, there are many places where the framework sequence is much extended or "filled-out", as it were, by an abundance of lavas and tuffs which are peculiar to the respective localities of occurrence, and which sometimes present unusual features.

This is particularly the case with the Eelah-Gosforth District (Browne, 1926) and the Stanhope District (Scott, 1947). In the former there are acid rocks below the andesites of the Volcanic Stage, and there is a repetition of hornblende and pyroxene andesite units. In the Stanhope District a remarkable development of intermediate and acid rocks underlies those lavas which throughout the Lower Hunter, are regarded as marking the beginning of eruptions in the Volcanic Stage.

##### *Correlations of the Sequences in the Lower Hunter Areas.*

Not much has been published regarding the correlation of outstanding lavas and tuff horizons in the Lower Kuttung Series, although various workers

have had the subject much in mind, and considerable discussion has been engaged in, so that some ideas have become fixed regarding the equivalence of certain indicator horizons in separated localities.

Sussmilch (1923) set up certain correlations of sections in the Volcanic Stage but made some deductions which have proved erroneous. Browne (1926) explained certain broad correlations between the Gosforth District and the type areas further east. Miss Scott (1947) attempted to effect some detailed correlations between the Stanhope-Gosforth area and the type-area, and illustrated her views with columnar sections. In regard to these the author would venture the opinion that not all the suggested correlations are correct. First, though the basal andesites of the Volcanic Stage in the Seaham-Clarencetown area are correctly linked with similar flows at Gosforth and Stanhope, the higher andesites found in the latter places have no counterparts in the type-area. Secondly, in spite of his original statement (Osborne, 1922, 167) the author is not now satisfied that the Basal Stage as exposed in the type-area is present at Gosforth and Stanhope, since the sequence so designated there by Miss Scott has hitherto yielded no traces of the characteristic flora. It includes a number of lava-flows, and is perhaps better regarded as a downward extension of the Volcanic Stage.

The following correlations are given here as a result of mature consideration of the Kuttung succession across the whole of the Lower Hunter-Karuah region

(1) *The Martin's Creek Andesite Horizons (lithoidal and glassy)* may be traced from the Girvan District, on the east, through the Volcanic Stage belt which runs along the western side of the Stroud-Gloucester Trough. The andesite outcrops on the roadside about six miles east of Dungog and continues southwards to Clarencetown. (Beyond this point the regional distribution in the type area has already been published.) It can then be traced northward from Paterson towards Gresford, and suffers much faulting between this locality and Gosforth-Stanhope. The strict correlation in the latter area equates the horizons on the lower slopes of Hudson's Peak with those of Martin's Creek. These horizons of Hb. Andesite do not occur to the west or north of the Cranky Corner-Glendonbrook district. The intervention of the Webber's Creek fault and the Hunter Thrust have cut out possible extensions.

(2) *The Hudson's Peak type of pyroxene andesite and pitchstone* can be traced almost as satisfactorily as the amphibole types. The areas of greatest development are at Hudson's Peak, Stanhope and Balikera, near Seaham. West of the Stanhope area there are several flows of this type in the areas near the Hunter Thrust Line and elsewhere. In almost every case the associated strata indicate the validity of correlating them with the lower units found on Hudson's Peak.

(3) *The Williams River Quartz Keratophyre* is an intensely albitised dacite or toscanite, according to the area chosen. It does not occur in the Karuah Valley but can be traced from Limeburner's Creek through the complexly-faulted areas westward to Vacy and Gresford, eventually to appear at Eelah, Gosforth and Stanhope, being the first important flow to succeed the upper Hb. Andesites of those districts. Beyond this locality this horizon is absent from the sequence.

(4) *The Mt. Gilmore Toscanite-Dellenite Group*, over a wide area, has been proved a most reliable stratigraphical index.

This horizon varies through a limited range of composition, and also varies somewhat in texture, but is mostly medium to coarse-grained in its phenocrystic content.

A great development of this unit is seen around the nose of the Girvan anticline, east of Booral, and especially also along its western side. Thus the

rugged hills flanking the Lower Karuah River on the east side are made of thick flows of this rock. The dominant ridges of toscanite on either side of the Stroud-Gloucester Trough are directly to be correlated with the Mt. Gilmore horizon.

Beyond the type area, the toscanite is found strongly developed at Belah Gap and along the Rosebrook Ridge westward to Stanhope. West of Glendonbrook it peters out and is unknown from the great areas of Volcanic Stage rocks in the middle Hunter Valley.

With few exceptions we cannot confidently correlate the many horizons of dacite, soda rhyolite, potash rhyolite and sodi-potassic types across areas of significant dimensions. Some very local linkings can be made, of course. The main point to emphasise, however, is that acid and sub-acid rocks are characteristic, as a group, of the top of the Volcanic Stage.

#### (b) *The Middle Hunter Region.*

The Kuttung Belt which outcrops along the north-eastern side of the Middle Hunter Valley displays a sequence in the Volcanic Stage which is distinctly different from that of the areas dealt with above.

The important Kuttung areas in the Middle Hunter region are the Mirrannie-Dyrring, Glennie's Creek-Muswellbrook and the Mid-Rouchel-Bowman's Creek districts.

The framework sequence is incomplete because of the truncating effect of the Hunter Thrust all along the bounding zone between Glendonbrook and Muswellbrook.

The chief features of the sequence are :

- (a) The presence of the pyroxene andesite in the lower stratigraphical zones.
- (b) The abundance of *ignimbrites*, viz. on four main horizons, previously described as the Bridgman, Sedgfield, Westbrook and Glendonbrook Felsites (Osborne, 1926).
- (c) The concentrated incidence of dacites a little above the topmost *ignimbrite*.
- (d) The remarkably constant development of flows of typical Hb. Andesite at the top of the Volcanic Stage.

The skeleton sequence, therefore, is as follows, proceeding from older to newer : pyroxene andesites, ignimbrites, dacites and hornblende andesitic pitchstones. Various local modifications occur in this province, the chief examples being (a) the development of a group of spherulitic lavas in the Cross Creek area, north-west of Singleton, and (b) the appearance of an extra group of hornblende andesites in the Muscle Creek Section.

#### LOWER KUTTUNG TUFFS, FLOW-BRECCIAS AND RELATED TYPES.

Throughout the Lower Kuttung there is a great development of true pyroclastic rocks and of tuffaceous deposits which are due to admixture of ash and sedimentary units accumulated mainly sub-aqueously, but occasionally in a piedmont environment. The more strictly igneous of the tuffaceous groups are medium to fine-grained, and show wide variation of composition, with a preponderance of biotite-dacite tuff in the lowermost zones and a predominance of soda-rhyolite tuff in the upper levels of the succession.

The totally pyroclastic rocks comprise (a) autobrecciated rhyolites, dacites and felsites, and (b) agglomerate and breccia formed by the accumulation of falling fragments from paroxysmal eruptions of fairly restricted extent.

Since recording in earlier papers the occurrence and petrography of many of these clastic rocks, the writer has been assembling data concerning their relationships with the facts of sequence and composition of the flows in the various neighbourhoods.

It can now be assumed that specialised centres of eruption have been responsible for great variety and overlapping of small flows in areas where flow-breccias and shatter-agglomerates are developed.

Following this line of enquiry it now becomes possible to postulate centres of eruption having considerable influence in overlapping, yet not controlling the distribution of the leading flows of the framework sequence.

Thus, partly based on the evidence of the tuff and breccia occurrences, we recognise the following centres in the Lower Kuttung :

- (a) Muscle Creek, east of Muswellbrook.
- (b) Cross Creek, north of Singleton.
- (c) Bridgman District.
- (d) Mirannie Area.
- (e) Breckin Area.
- (f) Gosforth District.
- (g) Stanhope District.
- (h) Pokolbin District.
- (i) Martin's Creek District.
- (j) Glenoak District.
- (k) Mt. Gilmore, near Clarencetown.
- (l) Booral and East Stroud.
- (m) North Stroud-Weistmantels.

All through the present discussion it has been assumed that the framework sequence which holds so well over widespread localities, covering as much as 3,000 square miles, is the expression of a regional magmatic differentiation, and a regional control in serial eruptions, based upon widespread fissuring throughout large tracts whose geotectonic condition was related to a tensional environment, dependent upon gravity or isostatic controls.

#### VULCANICITY OF THE UPPER KUTTUNG SERIES.

The chief features of the volcanic succession in the Upper Kuttung Series in the region under notice are :

- (i) The widely developed toscanite-dellenite lavas of the Paterson Type, which occupy a constant stratigraphical position.
- (ii) The specialised occurrence of varied lava sequences in the upper part of the Glacial Stage.

It is clear that the Paterson lavas and associated pumiceous tuffs indicate the widespread revival of volcanic activity marked by fissure eruptions of a toscanite almost identical with an earlier fissure product (the Mt. Gilmore Toscanite). The Paterson Type has been studied from the whole of the Kuttung Belt lying between Raymond Terrace and the Mirrannie-Bowman's Creek region. Beyond this the flows die out and are absent from the Upper Hunter Kuttung areas. The rocks grade from toscanite to dellenite, but as a group are markedly constant, petrologically.

High up in the Glacial Stage at Pokolbin, and also at Stanhope and Stroud, there is a noteworthy development of lavas embracing alkaline types such as trachyte and trachy-basalt, also flows of basalt. Small amounts of basalt have been recorded from elsewhere, but in the Stroud-Weistmantels sector there is a strong development of the basic rock.

It is clear that towards the end of Kuttung time there was developed, in response to local stress conditions, a series of strongly differentiated centres of

magmatic activity, by which the usual calcic series of andesite-dacite-rhyolite was modified by the incoming of alkaline types. At the same time basalts with alkaline affinities began to appear. Until considerable chemical and petrological information regarding these basalts is forthcoming it would be inadvisable to endeavour to relate them to the Kuttung sequences.

The presence of ignimbrites in the Glacial Stage at Stroud is a feature of Kuttung vulcanicity hereabouts. Two horizons are well represented (see section below). The outcrops of the upper ignimbrite to the west of the Pacific Highway about  $1\frac{1}{2}$  miles south of Stroud Road recall vividly the field appearance of the well-known New Zealand type, Wilsonite, described by Marshall.

#### CHEMICAL ANALYSES

Below is given a list of analyses of representative lava-members of the Kuttung Succession. It is to be regretted that no unit which can be confidently interpreted as an ignimbrite has been analysed. No worth-while petrogenic discussion of the Kuttung lavas is yet possible, because so many of the rocks have been profoundly altered by deuteric processes, especially that of *albitisation*. Until a much greater amount of chemical data is available, one deprecates any attempt to discuss, more or less comprehensively, the chemical problems of the Kuttung vulcanicity.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
SiO <sub>2</sub> ..	64.20	64.88	61.10	67.06	73.04	73.90	72.98	77.82	75.06
Al <sub>2</sub> O <sub>3</sub> ..	16.88	16.18	16.20	15.95	13.86	11.95	12.58	11.46	14.21
Fe <sub>2</sub> O <sub>3</sub> ..	1.90	1.52	2.00	1.78	1.60	1.70	0.28	0.30	1.31
FeO ..	2.52	2.43	3.78	2.37	0.45	0.99	1.66	0.09	0.27
MgO ..	0.66	1.21	3.55	1.87	0.48	0.55	0.49	0.23	0.09
CaO ..	3.14	3.00	4.90	1.98	1.44	1.50	2.81	0.22	0.42
Na <sub>2</sub> O ..	4.41	5.41	3.42	4.62	3.40	3.10	4.80	0.86	6.88
K <sub>2</sub> O ..	3.52	2.79	2.83	2.01	4.39	4.74	2.99	7.19	0.58
H <sub>2</sub> O+	1.79	1.63	1.03	0.65	0.79	1.37	0.79	1.40	0.62
H <sub>2</sub> O—	0.31	0.50	0.53	0.44	0.25	0.21	0.43	0.36	0.56
CO <sub>2</sub> ..	0.03	tr.	abs.	abs.	abs.	abs.	abs.	0.03	—
TiO <sub>2</sub> ..	0.65	0.89	0.55	0.40	0.22	0.20	0.40	0.02	abs.
P <sub>2</sub> O <sub>5</sub> ..	0.13	tr.	0.21	0.28	0.04	0.05	0.08	0.04	0.03
MnO ..	—	0.05	tr.	0.39	0.07	0.06	0.03	tr.	0.04
BaO ..	—	—	tr.	—	0.04	0.06	—	0.02	—
etc.									
	100.14	100.49	100.10	99.80	100.07	100.38	100.32	100.04	100.07

- I. Hb. Andesite, Martin's Creek. Anal. G. D. Osborne.  
 II. Hb. Andesite, Martin's Creek. Anal. W. G. Stone.  
 III. Pyroxene Andesite (Hudson's Peak Type), Pokolbin. Anal. W. A. Greig.  
 IV. Qtz. Keratophyre (Williams River Type), Clarencetown. Anal. G. D. Osborne.  
 V. Toscanite, Mt. Gilmore. Anal. W. A. Greig.  
 VI. Toscanite (Mt. Gilmore Type), Port Stephens. Anal. W. G. Stone.  
 VII. Toscanite, Paterson. Anal. G. D. Osborne.  
 VIII. Rhyolite, Mt. Bright, Pokolbin. Anal. J. C. H. Mingaye.  
 IX. Soda Rhyolite, Paddy's Hill, north of Raymond Terrace. Anal. W. A. Greig.

#### THE IGNIMBRITES.

##### *Previous Recognition of Ignimbrites in the Kuttung Succession.*

In 1923 the writer visited New Zealand and studied the occurrence and petrography of the ignimbrites of the North Island, after the advantage of full discussion of these rocks with Dr. P. Marshall, who first interpreted the rhyolitic

rocks of the Great Volcanic Plateau as compacted material ejected as *nuées ardentes* (Marshall, 1932). Subsequently, in 1934, in an address to the Geological Section of the Royal Society of N.S.W. upon the N.Z. ignimbrites (see *THIS JOURNAL*, Vol. 68, p. xlviii), specimens of certain Kuttung rocks were exhibited and the opinion expressed that these were ignimbrites.

Quite recently Beryl Scott (1947) has recorded the presence of ignimbrites in the Volcanic Stage in the Stanhope District, and has given somewhat meagre metrographic accounts of these.

Since suggesting an ignimbritic origin for many of the volcanic units hitherto described from the Kuttung as rhyolites, and rhyolitic tuffs, the writer has been assembling evidence of the widespread occurrence of these fascinating rocks in the Hunter and Karuah River Districts.

(It is pertinent to mention here that in 1934 H. C. Richards and W. H. Bryan discussed the mode of origin of part of the Brisbane Tuff and concluded that it paralleled very closely the ignimbrites of New Zealand.)

#### *Field Occurrence.*

The ignimbrites of the N.S.W. Carboniferous are distinctive in their field relations, occurring in relatively thin units which are remarkably persistent over large areas. The thickness varies up to a maximum of 120 feet, but generally is small and of the order of 12–20 feet. The rocks are light coloured with marked “fluidal” texture, and show in many areas a rude prismatic jointing more or less perpendicular to the “flow structure”. This jointing does not pass into the associated rocks, nor is it related genetically to any tectonic features of the surrounding country. It is essentially syngenetic, and this recalls the prevalence of syngenetic jointing in the New Zealand ignimbrites. Marshall interprets this as evidence against a rock with flow structure consolidating from a molten condition. (It is interesting to note that in several early papers published by the writer before the concept of ignimbrites was forthcoming, reference to this jointing was made, although its significance was not known.)

It always has been difficult to explain the “flow” structures and the extremely extended outcrops of the ignimbrites, if they were to be regarded as acid flows. With high viscosity characteristic of the rock-types under consideration, considerable flowing of the magma would have been unlikely, and the regularity of the flow-layers would almost certainly have been obliterated or modified by flow-breccia structures.

In two or three places in the Middle Hunter area it is possible to see evidence that the ignimbrite was developed on a very uneven floor, and reconstruction of the physiography of the localities in question indicates that the igneous rock (if a flow) travelled “uphill” considerably. With more and more field work in recent years, it has become necessary to invoke some special mode of development different from accepted ideas of the ordinary flow of lava, to explain the units now being discussed. Accordingly I have concluded that the rocks in question have had essentially the same mode of origin as the ignimbrites described by Marshall. Some fuller explanation of this view is given below.

#### *Petrography.*

The ignimbrites vary in grainsize, and may be very heterogeneous on a small scale, while at other times exhibiting an even-textured “ground” through which are strung axiolites, beaded concentrations of spherulites, and comb-like structures in fibrous feldspathic and siliceous material. Many shards and tubes of pumice and myriad cusped fragments and shreds of glassy material are packed into a solid mass with pseudo-fluidal texture, giving distinctive fracture and variable lustre from surface to surface.

## LOWER KUTTUNG IGNIMBRITE HORIZONS

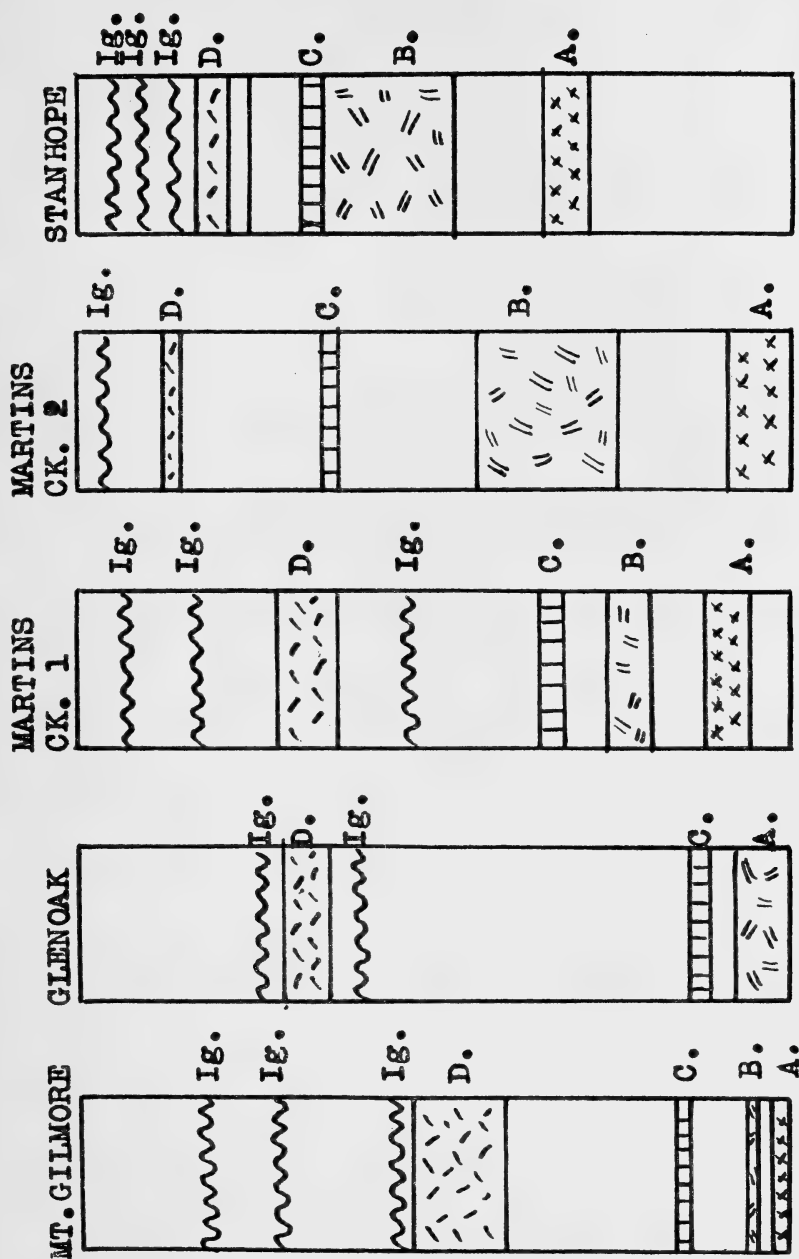


Fig. 1.—A. signifies Martin's Creek horizon. B. Hudson's Peak horizon. C. Williams River horizon. D. Mt. Gilmore horizon. Ig. Ignimbrite. Thickness of sections given in text. (Note.—In the Glenoak Section the lowest unit should be marked B, not A.)

There is a suggestion of dense silicification or of devitrification in many rocks. While patches are glassy, the bulk of the rocks are now lithoidal or felsitic.

The rocks show no scoriaceous or ropy texture at the upper surface, although the apparent flow structure is so marked in the body of the rock. Uniformity of colour (mostly pink or cream) is a feature over wide areas and there is an absence of abrupt passage from fluidal rock into brecciated material, such as is seen with many of the normal Kuttung flows. No autoclastic structure or twisted flow-fabric occurs in the ignimbrites, such as is seen in modern lavas whose origin is not in doubt.

*Microscopically*, the ignimbrites are very difficult of satisfactory study, and it is not proposed to discuss the petrography in full, as this will be taken along with a chemical study of these rocks in the future. It is sufficient to note that the "phenocrystic" minerals commonly developed are quartz, oligoclase or albite, biotite, and a variable amount of orthoclase. Rarely altered hornblende is seen, and occasionally one or two pieces of what appear to be hypersthene. These units (of approximately uniform grainsize up to a maximum of 2 mm.) are set in a devitrified pumiceous groundmass of fine silica and felspathic material, through which are threaded abundant axiolitic and genetically kindred structures.

Many of the tubular or shred-like fragments bend around the "phenocrysts" of albite and quartz and indicate clearly a plastic condition prior to crystallisation.

### *Stratigraphical Horizons.*

Text-figure 1 indicates the stratigraphical relationships of the ignimbrite deposits, the chronological positions of the postulated eruptions being summarised thus :

- (a) There is a pronounced concentration towards the upper part of the Volcanic Stage, the Stanhope Section being the only one in which an ignimbrite has been recorded from low down in the sequence.
- (b) Within the Volcanic Stage most of the ignimbrites are above the horizon of the Mt. Gilmore toscanite although in two sections an ignimbrite zone marks the infra-toscanite series.
- (c) In the Glacial Stage there are two ignimbrite horizons, these being respectively below and above the horizon of the Paterson toscanite.

It would thus appear that the special eruptive conditions for the production of ignimbrites obtained at several distinct times in the areas now being considered. These violent conditions occurred in the Upper Volcanic Stage and the Mid-to-Upper Glacial Stage.

### DETAILED STRATIGRAPHICAL SECTIONS SHOWING IGIMBRITE HORIZONS.

It is proposed in this section to restate certain sections of the Volcanic Stage, already published, and to record a new section from the Glacial Stage, for the purpose of placing on record the stratigraphical positions, and the stratigraphical concentration of ignimbrites in the Kuttung succession. (All sections descend stratigraphically.)

(a) *The Mt. Gilmore Section* (Osborne, 1922, p. 172).

	Feet
Tuffs .. .. .	45
Volcanic conglomerate .. .. .	50
Tuffs with pebbly bands .. .. .	130
Potash rhyolite .. .. .	50
<i>Ignimbrite</i> .. .. .	50
Conglomerate .. .. .	80
Potash rhyolite .. .. .	40
Conglomerates .. .. .	90



Keratophyre .. .. .	90
Conglomerate .. .. .	50
<i>Ignimbrite</i> .. .. .	100
Red potash rhyolite .. .. .	60
Conglomerate .. .. .	150
<i>Ignimbrite</i> .. .. .	70
Tuffaceous conglomerate .. .. .	45
<i>Ignimbrite</i> .. .. .	60
Tuffs with felsite .. .. .	80
Dellenite-Toscanite (Mt. Gilmore Type) .. .. .	400
Conglomerate .. .. .	320
Rhyo-dacite .. .. .	150
Bi. Qtz. keratophyre (Williams River type) .. .. .	105
Conglomerate .. .. .	30
Bi. Qtz. keratophyre (Williams River type) .. .. .	150
Conglomerate .. .. .	75
Sodi-potassic rhyolite .. .. .	45
Conglomerate .. .. .	80
Pyroxene andesite (Hudson's Peak type) .. .. .	50
Pebbly tuff .. .. .	150
Hornblende andesite (Martin's Creek type) .. .. .	80
Total .. .. .	2,875

(b) *The Glenoak Section* (Osborne, 1922, p. 175).

	Feet
Dacite .. .. .	120
Sodi-potassic rhyolite .. .. .	45
<i>Ignimbrite</i> .. .. .	130
Rhyolite .. .. .	250
Dellenite (Mt. Gilmore type) .. .. .	80
Conglomerate .. .. .	45
<i>Ignimbrite</i> .. .. .	40
Fine-grained quartz keratophyre .. .. .	90
Conglomerate .. .. .	450
Felsite .. .. .	60
Conglomerate .. .. .	180
Fine tuff .. .. .	60
Coarse tuff .. .. .	100
Volcanic conglomerate, etc. . . . .	60
Bi. Qtz. keratophyre (Williams River type) .. .. .	180
Pebbly tuff .. .. .	100
Pyroxene andesite glass (Hudson's Peak type) .. .. .	200
Total .. .. .	2,190

(c) *Martin's Creek, Section No. 1* (Osborne, 1922, p. 177).

	Feet
Tuffs .. .. .	200
<i>Ignimbrite</i> .. .. .	30
Dacite .. .. .	100
Flow-breccias .. .. .	80
<i>Ignimbrite</i> .. .. .	25
Pebbly tuff .. .. .	185
Toscanite (Mt. Gilmore type) .. .. .	210
Tuffaceous conglomerate .. .. .	200
<i>Ignimbrite</i> .. .. .	80
Tuff .. .. .	70
Conglomerate .. .. .	65
Bi-Qtz. keratophyre (Williams River type) .. .. .	85
Conglomerate .. .. .	100
Pyroxene andesite (Hudson's Peak type) .. .. .	80
Pebbly tuff .. .. .	100
Hornblende andesite (Martin's Creek type) .. .. .	200
Total .. .. .	1,810

(d) *Martin's Creek, Section No. 2* (Osborne, 1922, p. 178).

	Feet
<i>Ignimbrite</i> .. .. .	50
Cherty tuff .. .. .	25
Fine-grained tuffs .. .. .	15
Volcanic conglomerate .. .. .	10
Conglomerate .. .. .	15
Toscanite (Mt. Gilmore type) .. .. .	50
Soda-felsite .. .. .	100
Red potash-rhyolite .. .. .	25
Coarse conglomerate .. .. .	300
Bi-Qtz. keratophyre (Williams River type) .. .. .	50
Total .. .. .	640

(e) *The Stanhope Section* (Scott, 1947).

	Feet
Dacite tuffs with several <i>Ignimbrite</i> horizons (relatively thin) .. .. .	800
Toscanite (Mt. Gilmore type) .. .. .	260
Conglomerate .. .. .	180
Toscanite (on horizon of Williams River keratophyre) .. .. .	400
Hornblende andesite .. .. .	900
Pyroxene andesite (Hudson's Peak type) .. .. .	1,200
Conglomerate .. .. .	350
Hornblende andesite (Martin's Creek type) .. .. .	130
Conglomerate .. .. .	160
<i>Ignimbrite</i> .. .. .	30
Conglomerate .. .. .	250
Felsite .. .. .	130
Fluvio-glacial conglomerate .. .. .	450
Pyroxene andesite .. .. .	50
Conglomerate .. .. .	50
Rhyolite .. .. .	920
Pyroxene andesite .. .. .	660
Conglomerate .. .. .	100
Rhyolite .. .. .	?
Total, at least .. .. .	7,020

(f) *The Bridgman Section* (Osborne, 1926, p. 391).

	Feet
Hornblende andesite .. .. .	200
Conglomerate and tuff .. .. .	150
Hornblende andesite .. .. .	50
Conglomerate .. .. .	170
Hæmatitic flow-breccia .. .. .	20
<i>Ignimbrite</i> .. .. .	30
Felsite .. .. .	15
<i>Ignimbrite</i> .. .. .	20
Conglomerate with hæmatitic lava band .. .. .	250
<i>Ignimbrite</i> .. .. .	30
Conglomerate .. .. .	220
<i>Ignimbrite</i> .. .. .	30
Conglomerate and tuffs .. .. .	150
<i>Ignimbrite</i> .. .. .	40
Conglomerate and tuff .. .. .	60
Total .. .. .	1,435

(g) *The Muscle Creek Section* (Osborne, 1928, p. 568).

	Feet
Tuffaceous conglomerate .. .. .	300
Felsite .. .. .	80
Tuffaceous conglomerate .. .. .	200
Dacite .. .. .	100
Coarse conglomerate .. .. .	400
Biotite felsite .. .. .	50

Conglomerate .. .. .	300
Hb. andesite glass .. .. .	80
Conglomerate .. .. .	200
Fine tuff .. .. .	300
Coarse tuff .. .. .	100
Acid tuff .. .. .	170
Conglomerate .. .. .	100
Andesitic conglomerate .. .. .	90
Soda felsite .. .. .	60
Conglomerate .. .. .	200
Tuff .. .. .	80
Dacites (devitrified) .. .. .	245
Tuff .. .. .	100
<i>Ignimbrite</i> .. .. .	120
Coarse tuff .. .. .	300
<i>Ignimbrite</i> .. .. .	150
Tuff and conglomerate .. .. .	200
Dacite .. .. .	170
Tuff and conglomerate .. .. .	95
<i>Ignimbrite</i> .. .. .	85
Tuff .. .. .	200
Soda felsite .. .. .	90
Tuff and conglomerate .. .. .	230
Total .. .. .	4,795

## (h) The Stroud Section (Generalized).

	Feet
Basalt .. .. .	200
Andesitic tuff .. .. .	150
<i>Ignimbrite</i> .. .. .	25
Conglomerate .. .. .	20
Hb. andesite .. .. .	20
Rhyolite .. .. .	25
Dacite .. .. .	50
Coarse conglomerate .. .. .	30
Tuffs with pebbles .. .. .	560
Basalt .. .. .	150
<i>Rhacopteris</i> tuff .. .. .	20
Conglomerate .. .. .	100
<i>Ignimbrite</i> .. .. .	15
Sandy tuffs .. .. .	120
Total .. .. .	1,485

## MODE OF ORIGIN OF THE IGNIMBRITES.

It is the opinion of the writer that the ignimbrites here discussed have been formed after the manner described by Marshall for the N.Z. occurrences. That is to say they are due to the welding together of tuffaceous material given out in the incandescent state from fissures, and carried with swift velocity to places of accumulation. Thus they are the products of a series of *nuées ardentes*.

It is considered that the eruptions were of the *Katmaian Type*, in the nomenclature of Lacroix. This type, as opposed to the *Pelean* eruption (which takes place in a restricted crater) involves the supply of material from fissures. It is essential, in considering the origin of these fascinating rocks, that we should draw from the experience that scientists have had in observing modern eruptions of the "glowing cloud" or *nuée ardente* type. Fortunately the literature upon this subject is already considerable, and reputable geologists and petrologists have described phenomena observed by them, or have carefully investigated the recent products of outbursts of this kind. (See Flett, 1908; Jagger, 1903; Perrett, 1935; Lacroix, 1904; Macgregor, 1936, 1938; and Marshall, 1932, 1935). Thus we may postulate that shreds and chips of glassy material have

been produced by a frothing over and instantaneous shattering of pumiceous lava very rich in gas. Fairly large volumes of finely divided material have been involved in the accumulation of some of the thicker ignimbrites.

It is probable that in the areas of the Lower and Middle Hunter in Kuttung times there were alternations of eruptive controls, so that three types of vulcanicity affected the region from time to time. These were responsible at different epochs for

- (a) welling out of lava flows from fissures ;
- (b) explosive discharge of ash, pumice, tuffs, boulders, lapilli, etc., all at a temperature such that on falling to the ground no further vulcanological processes would be likely to continue ;
- (c) intensively gaseous and explosive eruptions of the *nuée ardente* type.

Apparently some of the products due to the second type of control would be pure tuffs or breccias while others would be contaminated by sediment. Very local eruptions would produce agglomerate and breccia-filled necks. In cases of eruptions of type (a), two cases would arise. Either homogeneous lava not greatly charged with volatiles would spread uniform flows over wide areas, or inhomogeneous lava would give rise to streaky and layered extrusions. Both products are encountered in the Kuttung fields, but the former is, of course, the prevalent type. An example of the latter is that of the heterogeneous felsite at the foot of the Hudson's Peak Section, near Gosforth.

#### *Prevalence of Gas in Ignimbrite Eruptions.*

Vulcanologists who have studied the origin and mode of accumulation of *nuées ardentes* emphasise that an important determining factor in the sudden development of an incandescent cloud from partly consolidated rock material and volcanic gases is the course of the gas-history in the time just prior to the climax of eruption. If gas is prevented from escaping from the vent, the lava is unrelieved by effervescence and the condition is reached when expansion produces a frothing pumice due to violent action breaking through any residual crust. Thus is caused the ejection of incandescent material. Reactions between liberated gases help to keep glowing the various fragments (large and small). Solidification of glassy blebs will set free gas, thus producing porous texture in some of the solid ingredients of a *nuée ardente*.

It is clear that the various grades of material which have frothed over will settle down in some sort of density-controlled stratification, even though the accumulation has been rapid and of avalanche character.

Rocks similar to the ignimbrites of New Zealand have been formed by recent or modern eruptions in the West Indies, Katmai Province of Alaska, Yellowstone National Park, Crater Lake (Oregon) and elsewhere (see Bibliography).

#### SUMMARY.

An account is given of the salient features of the Kuttung Vulcanicity in the Hunter-Karuah District, particular attention being given to the occurrence of welded pumiceous tuffs, known in New Zealand as *ignimbrites*. The stratigraphical incidence of the *ignimbrite* horizons is made clear by the statement of many detailed sections from the area. These fascinating units in the volcanic succession are shown by their features of (a) texture, (b) field occurrence, and (c) vulcanological environment, to correspond almost exactly to products of the Katmaian type of the *nuée ardente* type of eruption.

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